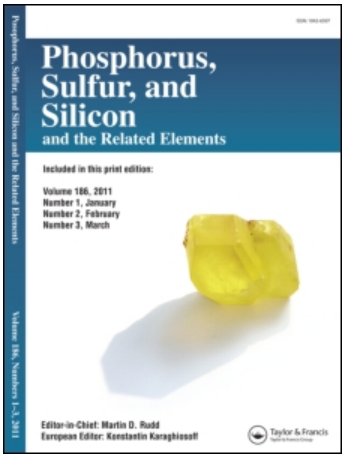

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTIONS OF TELLURIUM TETRAHALIDES WITH GLYCOLS

Ralph A. Zingaro[a]; Hema M. K. K. Pathirana[a]; Joseph H. Reibenspies[a]; Edward A. Meyers[a]
[a] Department of Chemistry, Texas A & M University, College Station, Texas, (U.S.A.)

To cite this Article Zingaro, Ralph A. , Pathirana, Hema M. K. K. , Reibenspies, Joseph H. and Meyers, Edward A.(1991) 'REACTIONS OF TELLURIUM TETRAHALIDES WITH GLYCOLS', Phosphorus, Sulfur, and Silicon and the Related Elements, 62: 1, 91 — 99
To link to this Article: DOI: 10.1080/10426509108034463
URL: http://dx.doi.org/10.1080/10426509108034463

Phosphorus, Sulfur, and Silicon, 1991, Vol. 62, pp. 91–99
Reprints available directly from the publisher
Photocopying permitted by license only

REACTIONS OF TELLURIUM TETRAHALIDES WITH GLYCOLS

RALPH A. ZINGARO, HEMA M. K. K. PATHIRANA, JOSEPH H. REIBENSPIES and EDWARD A. MEYERS

Department of Chemistry, Texas A&M University, College Station, Texas 77843 (U.S.A.)

(Received February 12, 1991; in final form April 19, 1991)

Tellurium tetrahalides undergo reaction with glycols to yield three different products: O,O′-dioxotrihalotellurates; *bis*(alkoxy)dihalotellurium (**IV**) compounds and hexahalotellurates. The course of the reaction appears to be determined primarily by the nature of the glycol. The structure of dichlorobis(*cis*-2-hydroxycyclohexyloxy)tellurium(**IV**) has been determined crystallographically.

Key words: tellurium; alkoxyhalotellurates; glycols; tellurium tetrahalides; immunoactivators.

INTRODUCTION

Büscher, Heuer and Krebs[1] reported the formation of tetraphenylphosphonium trichloro(1,2-dioxoethane-O,O′) tellurate(**IV**) by the reaction between 1,2-dihydroxyethane and tellurium tetrachloride and the subsequent addition of tetraphenylphosphonium ion. Albeck, Tamari and Sredni[2] reinvestigated this reaction and found that using acetonitrile as the solvent, the ammonium salt could be obtained directly. Sredni and co-workers[3,4] suggested that this compound possessed a chemical configuration similar to that of *cis*-dichloroethylenediamineplatinum (**II**). However, it must be recognized that the coordination numbers and coordination geometries of these two molecules differ significantly. Based on biological testing, they reported that the tellurium compound exhibited immunomodulatory activity both *in vitro* and *in vivo*. Recently, we found that when an alcohol is added to a solution containing $TeCl_4$ in N,N-dimethylformamide (DMF), there occurs an immediate displacement of the hydroxyl proton with the alkoxy group becoming bonded to tellurium and the concurrent formation of the hydrogen-bonded cationic species, $Me_2NC(H)O\cdots\overset{+}{H}\cdots O(H)CNMe_2$.[5] We were able to isolate the salt, $[DMF_2H]^+[EtOTeCl_4]^-$ and determined its crystal structure. The obvious similarities between our observations and those of Albeck, et al.[2] and Büscher and coworkers,[1] together with the interesting biological activity reported for compounds of this type, caused us to carry out a related study, the results of which are reported herein.

The preparation and characterization of several analogues are described and the structure of one is presented. The reaction has not been found to be general and the various products obtained with different alcohols are described in this paper.

RESULTS AND DISCUSSION

Following the procedure previously described,[2] we were able to prepare ammonium salts of the trichlorodioxotellurate ion, $[Cl_3Te(O_2C_2H_3R)]^-$, where R=H, $-CH_3$, $-C_2H_5$ and $-n-C_3H_7$. The data which served for the characterization of these compounds are included in the experimental section. This group of compounds was isolated in a routine manner, in pure form and without complications. However, with several other glycols, the reaction followed an entirely different course.

When the reaction was carried out with 2,3-dihydroxybutane, yellow crystals of ammonium hexachlorotellurate were easily identified. This salt, when allowed to react with an excess of the diol, a procedure used successfully in the synthesis of $(C_6H_5)_4P[Cl_3Te(O_2C_2H_4)]$,[1] did not convert to the trichlorodioxotellurate. It is of interest to note that when $TeBr_4$ was substituted for $TeCl_4$ in this reaction, the only product isolated with 1,2-dihydroxyethane or 1,2-dihydroxypentane was ammonium hexabromotellurate(**IV**).

Elemental tellurium was rapidly formed when $TeCl_4$ in acetonitrile was allowed to react with ethylenediamine, ethanolamine, N,N,N′,N′-tetramethylethylenediamine, fructose or 2-deoxy-*D*-glucose. It has been claimed[6] that the adjacent hydroxyl groups of monosaccharides coordinate with $TeCl_4$ in a manner similar to 1,2-dihydroxyethane, but this claim appears to be open to question.

Reaction Products Formed From Dihydroxycyclohexanes

When the reaction was carried out using *cis*- or *trans*-1,2-cyclohexanediol, colorless crystals separated from the reaction media which, in both cases, corresponded to the stoichiometry $[C_6H_{11}O_2]_2TeCl_2 \cdot 0.5CH_3CN$. The yellow filtrate, following evaporation of the solvent, yielded yellow crystals of $(NH_4)_2TeCl_6$.

The structures of the colorless crystals was unequivocally established. The presence of a nitrile group, inferred from the analysis, was corroborated by the presence of a sharp absorption at 2268 cm^{-1} in the infrared spectrum highly characteristic of $\nu(C{\equiv}N)$. Also, the ^1H nmr spectrum in CD_3OD displayed a sharp singlet at 2.0 ppm characteristic of the methyl group of acetonitrile. The question of the bonding between the tellurium atom and the oxygen atoms of the cyclohexanediol did not yield to ^1H nmr studies. This was because the compounds were not soluble in solvents such as acetonitrile and dimethylsulfoxide which could have established the presence or absence of a hydroxyl group at C11 or C12 (the numbering of the carbon atoms corresponds to those used in the crystal structure determination). The ^1H nmr studies, carried out in CD_3OD, did show the expected set of eight protons as a multiplet centered at 1.6 ppm (C13, C14, C15, C16) and a set of two protons bonded to C11 and C12 located at 4.09 ppm. Deuterium exchange obviated the identification of a free hydroxyl group at either C11 or C12. This resonance, for *cis*-1,2-cyclohexanediol, occurs at 2.80 ppm. The structure of the reaction product obtained from the reaction between $TeCl_4$ and *cis*-1,2-cyclohexanediol was established by x-ray crystallographic analysis and found to be dichlorobis(*cis*-2-hydroxycyclohexyloxy)tellurium (**IV**) · 0.5 acetonitrile. Unlike the compounds described earlier, only one hydroxyl proton from each molecule of the diol is displaced

while two of the chlorides to the tellurium (**IV**) have undergone nucleophilic displacement. The details of the structure are presented subsequently.

The crystal structure of the *trans*-derivative was not determined, but its stoichiometry is identical with that of the *cis*-derivative. Also, the infrared spectrum, $\nu(C{\equiv}N)$ at 2260 cm^{-1} and the ^1H nmr data are consistent with a structure which parallels that of the compound obtained with the *cis*-isomer.

Course of the Reaction

That the protons for the protonation of the nitrogen originate with the alcohol was established by carrying out the reaction with $DOCH_2CH_2OD$. The ^1H nmr spectrum of crystalline product formed, persumably $ND_4^+[Cl_3Te(—OCH_2CH_2O—)]^-$, showed no proton resonance otherwise present as a 1:1:1 triplet at 7.50, 7.24 and 6.99 ppm for the NH_4^+ ion. The ^1H nmr spectra of solutions of $TeCl_4$ in acetonitrile were measured as soon as possible following the addition of the diol. For example, the OH resonance of 1,2-dihydroxyethane can be observed at 4.406 ppm. Upon the addition of $TeCl_4$ this resonance disappears completely during the first few minutes, i.e., the time required to make the nmr measurement. Concurrently, there is observed the formation of the NH_4^+ triplet. Büscher, et al.,[1] explain the formation of $TeCl_6^{-2}$ primarily by dissociation of $TeCl_4$, i.e.,

$$3\ TeCl_4 \rightleftharpoons 2\ TeCl_3^+ + TeCl_6^{-2}$$

The dissociation of $TeCl_6^{2-}$ and subsequent reaction of $TeCl_5^-$ with the diol is proposed for the formation of the dioxotrichlorotellurate ion:

$$TeCl_6^{-2} \rightleftharpoons TeCl_5^- + Cl^-$$

$$TeCl_5^- + R(OH)_2 \rightleftharpoons Cl_3TeO_2R^- + 2\ HCl$$

We suggest that $TeCl_4$, itself, as evidenced by the formation $ROTeCl_4^-$[1,5] could undergo direct reaction with the diol:

$$TeCl_4 + R(OH)_2 \rightleftharpoons TeCl_4O_2R^{-2} + 2H^+$$

$$TeCl_4O_2R^{-2} \rightleftharpoons TeCl_3O_2R^- + Cl^-$$

The displaced chloride can add to $TeCl_4$ to form $TeCl_6^{-2}$. The formation of the latter has been observed in all of the reactions of $TeCl_4$ with alcohol which we have investigated.

In the case of cyclohexanediols, one of the alcoholic protons is retained and two of the chlorine atoms on $TeCl_4$ are displaced:

$$TeCl_4 + 2\ R(OH)_2 \rightleftharpoons Cl_4Te(OROH)_2^{-2} + 2H^+$$

$$Cl_4Te(OROH)_2^{-2} \rightleftharpoons Cl_2Te(OROH)_2 + 2Cl^-$$

$$2Cl^- + TeCl_4 \rightleftharpoons TeCl_6^{-2}$$

The interesting aspect of these reactions is the ease with which the very weakly acidic protons of the alcohols are abstracted under such mild conditions. We attribute this to the strength of the O—Te bond.

Albeck and co-workers[2] have suggested an interesting pathway for the formation of the ammonium ion when acetonitrile is present in this reaction. They suggest the halogenation of the diol to the halo alcohol, e.g., $HOCH_2CH_2Cl$. This reaction is accompanied by the formation of a mole of water. The reaction between acetonitrile and chloroethanol results in the formation of the iminoester, $H_3CC(=NH)OCH_2CH_2Cl$. The iminoester then undergoes reaction with water and HCl to form ammonium chloride. These investigators report the identification of 2-chloroethyl acetate and 2-chloroethyl propionate (when propionitrile is substituted for acetonitrile) in these reaction mixtures in support of the proposed pathway.

The reaction between alcohols and $TeCl_4$ is quite complex. The formation of alkoxychlorotellurates and hexachlorotellurates has been corroborated. The present work has also established the formation of dichlorobis(alkoxy)tellurium. Other tellurium compounds are formed, but their isolation, purification and unequivocal identification has eluded us. Also, no explanation is offered for our failure to synthesize analogues when 2,3-butanediol and 1,3-propanediol were used as alcohols.

Results of Biological Testing

The ammonioum salts having the anions $[Cl_3Te(O_2C_2H_3R)]^-$, where R = $—CH_3$, $—C_2H_5$ and $—n—C_3H_7$ were tested for activity against the Human Immunodeficiency Virus (HIV). The tests were performed at the National Cancer Institute and the procedure, based on formazan color development by viable cells has been described in detail.[7] The three compounds were found to be inactive. The rationale for testing these compounds was based on the reports of Sredni and co-workers.[3,4] These investigators reported that the analogue, $NH_4[Cl_3Te(O_2C_2H_4)]$, displays immunotherapeutic activity, but they employed a different test system. It would be of interest to evaluate the biological activity of the compounds prepared in this study in the systems used by these workers.

In evaluating the biological effects of this group of compounds, consideration must be given to their chemical fate upon their administration. Whether the biological evaluations are carried out either *in vitro* or *in vivo*, the compounds will enter an aqueous environment. It is well-known that the Te—Cl bond hydrolyzes readily and we have noted[5] that the RO—Te bond is extremely susceptible to hydrolysis. It is very unlikely, therefore, that the $[Cl_3TeO_2C_2H_3R]^-$ ion would survive in an aqueous environment. Rather, it would be rapidly converted to TeO_2 with the formation of intermediate species of the type $[Cl_nTe(OH)_m]^{-(m+n)+4}$. Hydrolysis of the Cl—Te bond would result in the formation of HCl.

EXPERIMENTAL

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. Me_4Si served as the internal standard. All shifts are reported in ppm. Infrared spectra were recorded in the form of KBr pellets using the IBM/FTIR/32 equipped with a DTGS detector. Uv-visible spectra were measured on the Varian DMS 100S spectrometer.

Tellurium tetrabromide was purchased from Pfaltz and Bauer. Tellurium tetrachloride and the dihydroxyalkanes were purchased from the Aldrich Chemical Co. All solvents were dried and redistilled prior to their use.

Analyses were performed by the Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of ammonium trichloro(1,2-dioxoethane-O,O')tellurate (**IV**) *using a sealed tube reaction.* Into a heavy walled glass tube bearing a constriction at one end was placed dry, powdered $TeCl_4$ (17.2 g, 64 mmol). Under an atmosphere of dinitrogen was added sufficient dried, redistilled acetonitrile to just dissolve the $TeCl_4$. Then 1,2-dihydroxyethane (9 ml, 160 mmol) was added. The glass constriction was flame sealed and the tube and its contents were heated at 92°C in an oven for four h. The tube was removed and allowed to remain at room temperature overnight. A crop of colorless crystals formed out of the yellow solution. These were removed by filtration and washed with cold acetonitrile. The crystals melted at 235°C (dec) (reported, 233°).[2] The yield was 9.13 g. The sealed tube method is simple and effective, but it was not used successfully for the synthesis of the other compounds.

Synthesis of perdeuteroammonium trichloro(1,2-dioxoethane-O,O')tellurate (**IV**). This compound was prepared in a manner identical to that immediately preceding using the sealed tube method. The only change was the substitution of ethylene glycol-d_2 for the 1,2-dihydroxyethane. The crystals, isolated in the same manner, were obtained in a yield of 10.5 g. They melted at 230°C (dec.). The ^1H nmr spectrum showed no resonances in the region of 7.0–7.5 ppm where the NH_4^+ triplet is normally observed.

Synthesis of ammonium trichloro(1,2-dioxopropane-O,O')tellurate (**IV**). A mixture of $TeCl_4$ (8 g, 30 mmol), 1,2-dihydroxypropane (5.4 ml, 74 mmol) and dry, redistilled acetonitrile (60 ml) was refluxed for four h under a dry dinitrogen atmosphere. The bright yellow solution was kept at room temperature for 16 h. A precipitate formed, off-white in color which was removed by filtration and washed with cold acetonitrile. The yield was 1.3 g of the salt which melted at 217°C (dec). Anal., calcd. (found) %, C, 11.05 (11.22); H, 3.16 (3.09); Cl, 32.62 (32.35); N, 4.29 (4.26). ^1H nmr: single protons at C1, 3.65 (t), 4.80 (q); single proton at C2, 4.35 (sept.); methyl group at C2, 1.23 (d); ammonium protons, 7.49, 7.23, 6.98.

Synthesis of Ammonium Trichloro(1,2-dioxo-n-butane-O,O')tellurate (**IV**). A mixture of $TeCl_4$ (5.9 g, 22 mmol), 1,2-dihydroxy-*n*-butane (5 ml, 56 mmol) and 45 ml of dry, redistilled acetonitrile was refluxed for four h under an atmosphere of dinitrogen. The solution was filtered and the bright yellow filtrate was kept in a refrigerator for 72 h. A colorless precipitate separated which was separated by filtration and recrystallized from acetonitrile. The recrystallized solid was stored over anhydrous $CaSO_4$ at reduced pressure. The yield of recrystallized product, m.p. 223°C (dec.), was 2.83 g Anal., calcd. (found) %, C, 14.09 (14.33); H, 3.83 (3.65); N, 4.11 (4.02). ^1H nmr: single protons at C1, 3.70 (t), 4.85 (q); single proton at C2, 4.25 (sext.); methylene group, 1.55 (quintet); terminal methyl group, 0.94 (triplet); ammonium protons, 7.50, 7.24, 6.99.

Synthesis of Ammonium Trichloro(1,2-dioxo-n-pentane-O,O')tellurate (**IV**). The procedure used paralleled exactly the two preceding. The quantities of reagents used were: $TeCl_4$ (8.1 g, 30 mmol), 1,2-dihydroxy-*n*-pentane (8 ml, 7.5 mmol), acetonitrile (60 ml). Following the reflux period and an extended period of cooling, no solid separated. The yellow solution was evaporated at reduced pressure until a heavy yellow oil remained. The heavy liquid, following an extended period of cooling, yielded a colorless precipitate which was separated from the yellow oil by filtration and washed with dry ether. The yield of the ammonium salt, m.p. 204° (dec.), was 4.45 g Anal., calcd. (found) %, C, 16.91 (17.43); H, 3.97 (4.01); N, 3.95 (4.01). ^1H nmr: single protons at C1, 3.70 (t), 4.80 (q); single proton at C2, 4.20 (sext.); methylene groups at C3, C4, 1.46 (mult.); terminal methyl group, 0.94 (triplet); ammonium protons, 7.51, 7.25, 7.00.

Synthesis of Dichlorobis(cis-2-hydroxycyclohexyloxy)tellurium (**IV**). A mixture of $TeCl_4$ (1.8 g, 7 mmol), *cis*-1,2-dihydroxycyclohexane (2 g, 17 mmol) and acetonitrile (20 ml) was refluxed at 92°C for four h under an atmosphere of dinitrogen. The formation of elemental grey tellurium was noted and this was removed by filtration at the end of the reflux period. The yellow filtrate was kept at room temperature for 16 h. Colorless crystals separated. These were separated by filtration and recrystallized from acetonitrile. The crystals, identified by crystallographic analysis as dichloro*bis*(*cis*-2-hydroxycyclohexyloxy)tellurium (**IV**) · 1/2 acetonitrile melted at 130°C. The yield was 1.15 g Anal., calcd. (found) %, for $C_{12}H_{22}Cl_2O_4Te \cdot 1/2\ CH_3CN$, C, 34.75 (34.78); H, 5.27 (5.77); Cl, 15.78 (15.97). ^1H nmr (see crystallographic section for identification of atoms): protons at C11, and C12, 4.09 (s); protons at C13, C14, C15, C16, broad multiplet at 1.61; hydroxyl proton at C12, 4.90 (s); methyl group of acetonitrile, 2.04 (s). The infrared spectrum showed a sharp C≡N stretching vibration at 2268 cm^{-1}.

Synthesis of Dichlorobis(trans-2-hydroxycyclohexyloxy)tellurium (**IV**). The reaction was carried out in a manner which paralleled that immediately preceding. *Trans*-1,2-dihydroxycyclohexane was substituted for the *cis*-isomer. The crystals which separated initially were washed with cold ether and recrystallized from acetonitrile. The yield of dichlorobis(*trans*-2-hydroxycyclohexyloxy)tellurium (**IV**) · 1/2 CH_3CN was 2.20 g. The compound melted at 163°C (dec.). Anal., calcd. (found) %, for $C_{12}H_{22}Cl_2O_4Te$ · 1/2 CH_3CN, C, 34.75 (35.00); H, 5.27 (5.21); Cl, 15.78 (15.55). ^1H nmr: protons at C11 and C12, 3.50 (s); protons at C13, C14, C15, C16, broad multiplet at 1.60; hydroxyl proton at C12, 4.90 (s); methyl group of acetonitrile, 2.04 (s). The fundamental C≡N stretching vibration was observed as a sharp band at 2260 cm^{-1}.

Synthesis of Ammonium Hexachlorotellurate. The synthesis of this compound was carried out according to the published procedure.[8] TeO_2 is dissolved in concentrated hydrochloric acid, the solution is evaporated and ammonium chloride is added. Evaporation of the solution yields bright yellow crystals of $(NH_4)_2TeCl_6$. Solutions of this compound in acetonitrile absorbed at 287.7 mμ, $\varepsilon = 6.7 \times 10^3$ and at 385.1, $\varepsilon = 4.8 \times 10^2$. In aqueous solution of HCl, the $TeCl_6^{-2}$ ion has been reported to absorb at 376 and 269 mμ,[9] but molecular extinction coefficients were not reported. Since different solvents were used, the differences are not unexpected.

Solutions of tetramethylformamidinium hexabromotellurate in acetonitrile absorbed at 319.8 mμ ($\varepsilon = 1.40 \times 10^4$) and at 446.3 m$\mu$ ($\varepsilon = 2.25 \times 10^3$). The yellow or orange solids which were separated from the various reaction mixtures possessed absorption spectra which very strongly support formation of the hexahalotellurate ion. From the reaction between *trans*-1,2-dihydroxycyclohexane, solutions of the yellow solid in CH_3CN absorbed at 385.0 and 287.0 mμ; from the reaction between 1,2-dihydroxyethane and $TeBr_4$, the orange solid in CH_3CN absorbed at 448.0 mμ and 329.0 mμ; from the reaction between 1,2-dihydroxypentane and $TeBr_4$, solutions of the orange solid which was separated absorbed at 447.6 and 329.4 mμ. In all cases the higher frequency absorption was the one of greater intensity.

From the reaction between 1,2-dihydroxy-3-bromopropane and $TeCl_4$, the orange-yellow solid which separated absorbed, in CH_3CN at 419.2 and 305.9 mμ. In this case the absorptions occur between those observed for salts containing the $TeCl_6^{-2}$ or the $TeBr_6^{-2}$ ions. We attribute this to the formation of the $TeCl_nBr_{6-n}^{-2}$ ion, but this has not been established with certainty.

Crystal Structure Determination of Dichlorobis(cis-2-hydroxycyclohexyloxy)tellurium (**IV**). The molecular structure of $C_{12}H_{22}Cl_2O_4Te$:0.5 CH_3CN has been determined by means of an X-ray diffraction study of a single crystal grown from a cooled solution of the compound in a mixed solvent consisting of a 1:1 (by volume) mixture of benzene and acetonitrile. A colorless prism of dimensions 0.06 mm × 0.09 mm × 0.28 mm was mounted with epoxy glue on a glass fiber and X-ray data collected from it at T = 293 K using a Siemens R3m/V diffractometer equipped with an oriented graphite monochromator. Unit cell dimensions were obtained from measurements of 2θ for 25 reflections with MoKα radiation, $\lambda = 0.71073$ Å. The crystal system is triclinic, P1 or $P\bar{1}$, with cell dimensions a = 8.028 (**1**) Å, b = 10.605 (**2**) Å, c = 10.918 (**2**) Å, $\alpha = 75.76$ (**1**) °, $\beta = 80.02$ (**1**) °, $\gamma = 78.71$ (**1**) °, V = 875.8 (**3**) Å^3. The unit cell contains two molecules of $C_{12}H_{22}Cl_2O_4Te$ and one molecule of CH_3CN:F (000) = 446, $\mu = 2.019$ mm^{-1}, $M_r = 898.6$, $D_x = 1.704$ Mg m^{-3}. Intensity data were collected for 3261, independent reflections: Wyckoff scans, scan speed varied from 1.00 to 14.65 degrees/minute, scan range 1.20° plus Kα separation, backgrounds measured before and after each scan each for 50% of the total scan time; $4.0° < 2\theta < 50°$, $-9 \le h \le 9$, $-12 \le k \le 12$, $0 \le 1 \le 12$. Three standard reflections were measured every 97 reflections, and a correction was applied to the data to compensate for a total loss of intensity of 11.4% during data collection. Two reflections, (0 1 0) and (0 $\bar{1}$ 0), were discarded because of interference from the beam stop ($2\theta = 4.01°$). For 139 of the 3259 intensities measured, $I \le \sigma(I)$ and for these reflections I was replaced by $\sigma(I)$. A semi-empirical absorption correction, based on ψ-scans, was applied to the data ($T_{min} = 0.7588$, $T_{max} = 0.8614$) as well as Lorentz and polarization corrections ($R_{int} = 2.41\%$).

A trial structure was obtained by direct methods and was refined in space group P1 by least-squares and Fourier calculations. The non-centrosymmetric space group was chosen because the statistical tests on functions of E favored it and because the centrosymmetric space group $P\bar{1}$ requires the acetonitrile molecule of solvation to be disordered. The two molecules of $C_{12}H_{22}Cl_2O_4Te$ present in the cell are so nearly related by a center of symmetry that the least-squares calculations continued to show oscillations in parameter values and disturbing variations in the bond distances after many cycles of refinement.

The refinement was then carried out in $P\bar{1}$. It converged quickly and satisfactorily and the results of these calculations are reported here. For all non-hydrogen atoms anisotropic and with H-atoms isotropic and placed in idealized positions in the cyclohexane groups (C—H = 0.96 Å), R = 0.0335, wR = 0.0364, 3259 reflections, 199 parameters goodness-of-fit = 0.99, quantity minimized $\Sigma w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma^2(F) + 0.0005\ F^2$. Refinement was terminated when the change in any parameter was less than 0.001 of its σ, and the final residual electron densities varied from 0.44 to -0.60 eÅ^{-3}. No attempt was made to place H-atoms bonded to O or present in the CH_3 portion of CH_3CN. Calculations were

done with SHELXTL PLUS.[10] Scattering factors were taken from the International Tables for X-Ray Crystallography.[11] The refined coordinates and equivalent temperature factors for the structure are listed in Table I. Bond lengths and bond angles are given in Table II and a stereoview of the structure is presented in Figure 1.

In the coordination around Te (IV), the axial Te—Cl and the equatorial Te—O bond distances and angles are typical of those found in other Te(IV) structures.[12] In addition, there are short Te . . . O

TABLE I

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U(eq)
Te(1)	8422(1)	2001(1)	9347(1)	29(1)
Cl(1)	6712(1)	2746(1)	7538(1)	62(1)
Cl(2)	10160(1)	1319(1)	11193(1)	44(1)
O(1)	6651(3)	2895(2)	10397(2)	34(1)
O(2)	6121(3)	309(3)	10717(3)	42(1)
C(11)	4928(4)	2565(3)	10681(4)	36(1)
C(12)	4955(5)	1159(4)	11444(4)	39(1)
C(13)	5470(6)	959(4)	12757(4)	50(2)
C(14)	4287(7)	1926(5)	13492(5)	62(2)
C(15)	4325(6)	3341(4)	12749(5)	53(2)
C(16)	3845(5)	3542(4)	11422(4)	47(2)
O(3)	9320(3)	3621(2)	8799(3)	35(1)
O(4)	11453(3)	1606(3)	7920(3)	43(1)
C(21)	11143(4)	3621(4)	8613(3)	33(1)
C(22)	12012(5)	2875(4)	7583(4)	39(1)
C(23)	11585(6)	3608(5)	6271(4)	52(2)
C(24)	12067(6)	4991(5)	5965(4)	57(2)
C(25)	11073(6)	5757(4)	6936(4)	52(2)
C(26)	11442(6)	5048(4)	8272(4)	48(2)
C(1AC)	10430(19)	135(12)	5254(12)	60(5)
C(2AC)	10088(38)	-724(22)	4470(21)	112(12)
N(1AC)	10734(20)	733(16)	5839(12)	86(6)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE II(a)

Bond lengths (Å)

Te(1)-Cl(1)	2.481 (1)	Te(1)-Cl(2)	2.529 (1)
Te(1)-O(1)	1.917 (2)	Te(1)-O(3)	1.913 (2)
O(1)-C(11)	1.455 (4)	O(2)-C(12)	1.443 (5)
C(11)-C(12)	1.517 (5)	C(11)-C(16)	1.516 (6)
C(12)-C(13)	1.514 (6)	C(13)-C(14)	1.536 (7)
C(14)-C(15)	1.523 (6)	C(15)-C(16)	1.518 (7)
O(3)-C(21)	1.442 (4)	O(4)-C(22)	1.444 (5)
C(21)-C(22)	1.525 (6)	C(21)-C(26)	1.523 (6)
C(22)-C(23)	1.514 (6)	C(23)-C(24)	1.532 (7)
C(24)-C(25)	1.516 (7)	C(25)-C(26)	1.517 (6)
C(1AC)-C(2AC)	1.483 (32)	C(1AC)-N(1AC)	1.087 (24)
C(1AC)-C(1AA)	1.074 (32)	C(1AC)-C(2AA)	0.775 (27)
C(2AC)-C(1AA)	0.775 (27)	C(2AC)-N(1AA)	0.794 (35)
N(1AC)-C(2AA)	0.794 (35)		

TABLE II(b)
Bond angles (°)

Cl(1)-Te(1)-Cl(2)	178.1(1)	Cl(1)-Te(1)-O(1)	90.7(1)
Cl(2)-Te(1)-O(1)	88.3(1)	Cl(1)-Te(1)-O(3)	88.3(1)
Cl(2)-Te(1)-O(3)	90.1(1)	O(1)-Te(1)-O(3)	86.7(1)
Te(1)-O(1)-C(11)	121.4(2)	O(1)-C(11)-C(12)	110.4(3)
O(1)-C(11)-C(16)	106.9(3)	C(12)-C(11)-C(16)	111.4(3)
O(2)-C(12)-C(11)	107.7(3)	O(2)-C(12)-C(13)	110.7(3)
C(11)-C(12)-C(13)	112.8(4)	C(12)-C(13)-C(14)	110.3(3)
C(13)-C(14)-C(15)	110.4(4)	C(14)-C(15)-C(16)	111.4(4)
C(11)-C(16)-C(15)	112.8(3)	Te(1)-O(3)-C(21)	120.6(2)
O(3)-C(21)-C(22)	110.0(3)	O(3)-C(21)-C(26)	108.1(3)
C(22)-C(21)-C(26)	112.2(3)	O(4)-C(22)-C(21)	107.4(3)
O(4)-C(22)-C(23)	110.4(4)	C(21)-C(22)-C(23)	112.2(3)
C(22)-C(23)-C(24)	109.9(4)	C(23)-C(24)-C(25)	110.0(4)
C(24)-C(25)-C(26)	110.7(3)	C(21)-C(26)-C(25)	113.0(4)
C(2AC)-C(1AC)-N(1AC)	177.4(17)	C(2AC)-C(1AC)-C(1AA)	30.2(14)
N(1AC)-C(1AC)-C(1AA)	152.3(21)	C(2AC)-C(1AC)-C(2AA)	135.7(23)
N(1AC)-C(1AC)-C(2AA)	46.8(26)	C(1AA)-C(1AC)-C(2AA)	105.5(31)
C(1AC)-C(2AC)-C(1AA)	44.3(23)	C(1AC)-C(2AC)-N(1AA)	132.0(28)
C(1AA)-C(2AC)-N(1AA)	87.7(32)	C(1AC)-N(1AC)-C(2AA)	45.4(21)

The atoms N(1AA), C(1AA) and C(2AA) are related to N(1AC), C(1AC) and C(2AC) respectively by the center of symmetry at (1, 0, 1/2).

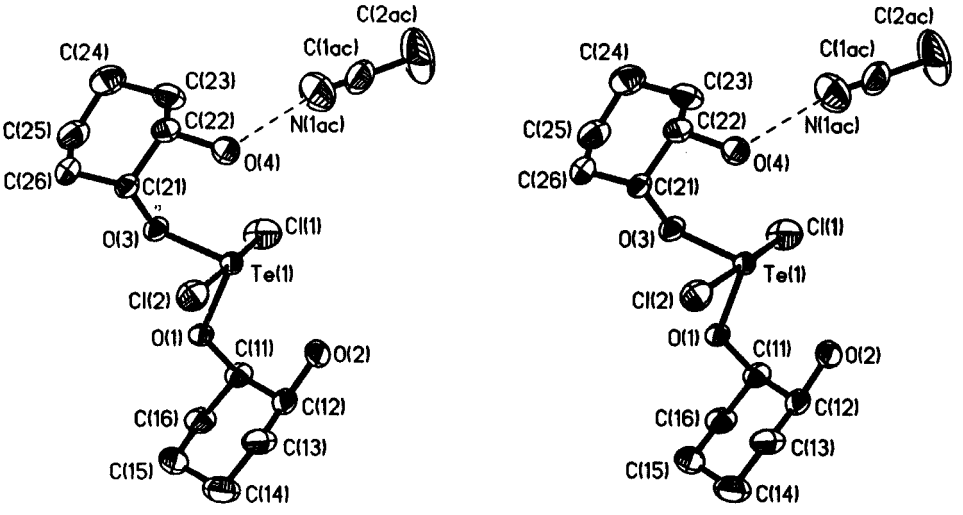

FIGURE 1 Stereographic views of dichloro*bis*(*cis*-2-hydroxycyclohexyloxy)tellurium (**IV**).

intramolecular contacts, Te (**1**) . . . O (**2**) = 2.81 Å and Te (**1**) . . . O (**4**) = 2.67 Å. The average C—O bond distance is 1.446 (**4**) Å and the average Te—O—C bond angle is 121.0 (**4**)°. The O atoms bonded to Te, O (**1**) and O (**3**), occupy axial positions in their respective cyclohexane rings and O (**2**) is cis- to O (**1**) and O (**4**) is cis- to O (**3**). The cyclohexane rings are in distorted chair configurations with average C—C = 1.520 (**2**) Å and average C—C—C = 111.5 (**3**)°. The torsion angles in ring [C (**11**) . . . C (**16**)] vary from +51.4 (**5**)° to −57.0 (**5**)°, and in ring [C (**21**) . . . C (**26**)] from +49.2 (**4**)° to −60.3 (**5**)°. It is assumed that one molecule of CH_3CN is present in each unit cell, located at either the positions given in Table I or at positions related to them by a center of symmetry. Since the CH_3CN molecule is disordered in this model, its bond distances and bond angles are the least reliable of those

calculated for this structure. There is a short contact between N(1AC) and O (**4**), 2.84 Å, and the angle O (**4**) . . . N(1AC) − C(1AC) = 163°, indicating the presence of a hydrogen bond interaction. If the disorder attributed to the alternative positions of the CH_3CN molecule is taken into account, there are no abnormal intermolecular contact distances.

ACKNOWLEDGEMENTS

We express our appreciation to the Robert A. Welch Foundation of Houston, Texas, and the Selenium-Tellurium Development Association for financial assistance in support of this work.

REFERENCES

1. K. Büscher, S. Heuer and B. Krebs, *Z. Naturforsch. Teil B*, **36,** 307–312 (1981).
2. M. Albeck, T. Tamari and B. Sredni, *Synthesis*, **8,** 635–636 (1988).
3. B. Sredni, R. R. Caspi, A. Klein, Y. Kalechman, Y. Danzinger, M. Ben Ya'akov, T. Tamari, F. Shalit and M. Albeck, *Nature*, **330,** 173–176 (1987).
4. B. Sredni, R. R. Caspi, S. Lustig, A. Klein, Y. Kalechman, Y. Danzinger, M. Ben Ya'akov, T. Tamari, F. Shalit and M. Albeck, *Nat. Immun. Cell Growth Regul.*, **7,** 163–168 (1988).
5. R. A. Zingaro, C. Herrera and E. A. Meyers, *Phosphorus, Sulfur and Silicon*, **48,** 1–10 (1990).
6. M. Albeck and B. Sredni, U.S. Patent 4, 764, 462, June 3, 1987.
7. O. W. Weislow, R. Kiser, D. Fine, J. Bader, R. H. Shoemaker and M. R. Boyd, *J. Natl. Cancer Inst.*, **81,** 577–586 (1989).
8. H. Marshal in "Inorg. Syntheses," II, W. C. Fernelius, ed., McGraw-Hill, New York, N.Y., 1946, p. 189.
9. M. W. Hanson, W. C. Bradbury and J. K. Carlton, *Anal. Chem.*, **29,** 490–91 (1957).
10. G. M. Sheldrick, Shelxtl Plus, Nicolet Instrument Corp., Madison, WI, USA—(1988).
11. "International Tables for X-ray Crystallography," Vol. IV, Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
12. M. M. Mangion, R. A. Zingaro and E. A. Meyers, *Chemica Scripta*, **8A,** 45–50 (1975).