**Table IX.** Ratio of $k(\mathrm{Cu})/k(\mathrm{Ni})$ for $ML^{2+}$ in 0.1 M HCl[a]

| | ligand | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| ring size | 14 | 15 | 16 | 17 |
| $k(\mathrm{Cu})/k(\mathrm{Ni})$ | 2.3 | $>8.8 \times 10^3$ | $>1.9 \times 10^4$ | $>1.7 \times 10^2$ |

[a] In 95% methanol at 25 °C.

ligand hole size with observed thermodynamic trends.

**Kinetics of Dissociation.** The kinetics of dissociation of the copper complexes in 95% methanol containing HCl ($I = 0.1$) have been studied. Table VIII lists the first-order rate data obtained when the dissociation of these complexes was followed in 0.1 M HCl as well as the rate for the complex of O-en-N-enH$_4$ in 0.05 M HCl; for this latter complex there is no significant difference between the observed rate constants for the two acid concentrations. A similar independence of acid concentration was observed for the dissociation of the corresponding complexes of nickel(II) both in 95% methanol and in aqueous media.[8] In all these cases it appears that the function of the acid is to scavenge the free ligand once it has dissociated from the copper ion (eq 3).

$$\begin{aligned} \mathrm{CuL}^{2+} &\rightarrow \mathrm{Cu}^{2+} + \mathrm{L} \quad \text{(rate determining)} \\ \mathrm{L} + 2\mathrm{H}^+ &\rightarrow \mathrm{LH_2}^{2+} \quad \text{(fast)} \end{aligned} \tag{3}$$

Comparison of the dissociation rates for the nickel and copper complexes of macrocycles **1**–**4** (Table VIII) reveals a striking example of kinetic discrimination between these metal ions. Specifically, for the 16-membered macrocycle, the dissociation rate of its copper complex is more than $1.9 \times 10^4$ times greater than that of its nickel complex, while for the 14- and 17-membered macrocycles it is only 2.3 and <170 times greater, respectively. Such discriminating ability undoubtedly reflects a number of factors, including the difference in covalent radii of the two ions and the likelihood that the copper ion sits out of the hole of the respective cyclic ligands—as discussed above for [Cu(O-en-N-tnH$_4$)Cl]ClO$_4$ in the solid state. Although some limited examples of related kinetic selectivity involving alkali and alkaline earth complexes of polyether-type macrocycles have been observed,[42] evidence for discrimination behavior of the type shown in Table IX involving different transition-metal ions has been quite rare.[5] Such data provide the foundation for the development of highly selective chromatography materials (macrocycles attached to insoluble supports) for transition-metal ions. Further work in this area is proceeding.

**Acknowledgment.** L.F.L. expresses thanks to the ETH, Zürich, for support during a period spent at the Laboratorium für Anorganische Chemie. Acknowledgment is made to the Australian Research Grants Committee for support and to the Australian Institute of Nuclear Science and Engineering for a travel grant. We wish to thank Dr. A. Ekstrom (Atomic Energy Commission, Sydney), Mr. B. Rüttimann (ETH, Zürich), and Dr. J. T. Baker (Roche Research Institute of Marine Pharmacology, Sydney) for assistance. M.M. and P.A.T. thank the Science Research Council (Warrington, U.K.) for diffractometer equipment and computing facilities.

**Registry No.** **1**, 65639-47-6; **2**, 65639-43-2; **3**, 65639-49-8; **4**, 66793-29-1; Cu(O-en-N-enH$_4$)(ClO$_4$)$_2$, 74261-95-3; Cu(O-en-N-enH$_4$)Cl$_2$, 74261-96-4; Cu(O-en-N-tnH$_4$)(ClO$_4$)$_2$, 74261-98-6; [Cu(O-en-N-tnH$_4$)Cl]ClO$_4$, 74262-00-3; Cu(O-en-N-tnH$_4$)Cl$_2$, 74310-47-7; Cu(O-tn-N-tnH$_4$)(ClO$_4$)$_2$, 74282-40-9; Cu(O-tn-N-tnH$_4$)Cl$_2$, 74262-01-4; Cu(O-bn-N-tnH$_4$)Cl$_2$, 74262-02-5; Cu(O-bn-N-tnH$_4$)Br$_2$, 74262-03-6; Ni(O-en-N-tnH$_4$)Cl$_2$, 66810-83-1; [Cu(O-en-N-tnH$_4$)$_2$][CuCl$_4$], 74262-05-8.

**Supplementary Material Available:** Listings of analytical data, full thermodynamic and kinetic data, a comparison of least-squares planes in the copper and nickel structures of macrocycle **2**, and structure factor tables for the copper complex are available (16 pages). Ordering information is given on any current masthead page.

---

[42] Cox, B. G.; Schneider, H. *J. Am. Chem. Soc.* **1977**, *99*, 2809. Cox, B. G.; Schneider, H.; Stroka, J. *Ibid.* **1978**, *100*, 4746.

---

Contribution from the Webster Research Center,
Xerox Corporation, Webster, New York 14580

# Crystal and Molecular Structure of Unsolvated Triphenyltelluronium Chloride, $(C_6H_5)_3TeCl$

RONALD F. ZIOLO* and MICHAEL EXTINE[1]

*Received February 13, 1980*

The structure of unsolvated triphenyltelluronium chloride, $(C_6H_5)_3TeCl$, has been determined by a single-crystal X-ray diffraction study. The salt crystallizes in the space group $P2_1/n$ of the monoclinic system with eight $(C_6H_5)_3TeCl$ units per cell. Lattice parameters (23 ± 1° C) are $a = 11.194$ (2) Å, $b$ 13.381 (2) Å, $c = 21.501$ (3) Å, $\beta = 104.51$ (1)°, and $V = 3117.8$ Å$^3$. The structure was solved by direct and Fourier methods from automatic diffractometer data collected on an Enraf-Nonius CAD4 using Mo K$\alpha$ radiation filtered by a graphite-crystal incident-beam monochromator. Refinement by the full-matrix least-squares technique led to a conventional $R$ factor (on $F$) of 0.023 for 6719 reflections having $F_o^2 > 3\sigma(F_o^2)$. Anisotropic thermal motion was assumed for the nonhydrogen atoms. Triphenyltelluronium chloride is dimeric and predominantly ionic in the solid state. Each tellurium atom is five-coordinate in a distorted square-pyramidal geometry. Two such square pyramids sharing a common basal edge through the bridging chloride ions compose the dimer. The dihedral angle between the pyramid bases is 129° and the axial Te–C vectors point in opposing directions. The Te–C distances are normal and have a mean value of 2.130 (4) Å. The Te–Cl interactions range from 3.142 (1) to 3.234 (1) Å, and the Cl–Te–Cl angles are 90.84 (2) and 92.28 (2)°. Two solvated compounds of the chloride have been identified, $(C_6H_5)_3TeCl \cdot {}^1/_2(C_2H_5)_2O$ and $(C_6H_5)_3TeCl \cdot {}^1/_2C_6H_6$, and unit cell data determined.

## Introduction

Recent studies on the triorganochalcogenonium salts, $R_3MX$, have shown that the salts have relatively complex structures due to weak bonding interactions between the chalcogen atom and the anion.[2-8] It has become evident that these interactions determine the overall structural features of

---

[1] Molecular Structure Corp., 3304 Longmire Dr., College Station, Texas 77840.

[2] Einstein, F.; Trotter, J.; Williston, C. *J. Chem. Soc. A* **1967**, 2018.

[3] Ziolo, R. F.; Pritchett, K. *J. Organomet. Chem.* **1976**, *116*, 211.

[4] Titus, D. D.; Lee, J.-S.; Ziolo, R. F. *J. Organomet. Chem.* **1976**, *120*, 381.

[5] Lee, J.-S.; Titus, D. D. *J. Cryst. Mol. Struct.* **1976**, *6*, 279.

0020-1669/80/1319-2964$01.00/0 © 1980 American Chemical Society

**Table I.** Crystal Data (23 ± 1 °C)

| compd | $(C_6H_5)_3TeCl$ | $(C_6H_5)_3TeCl\cdot{}^1/_2(C_2H_5)_2O$ | $(C_6H_5)_3TeCl\cdot{}^1/_2C_6H_6$ |
|---|---|---|---|
| space group | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$, Å | 11.194 (2) | 13.126 (3) | 13.402 (6) |
| $b$, Å | 13.381 (2) | 13.277 (5) | 14.568 (7) |
| $c$, Å | 21.501 (3) | 11.713 (8) | 10.484 (5) |
| $\alpha$, deg | 90 | 99.06 (4) | 98.64 (4) |
| $\beta$, deg | 104.51 (1) | 113.43 (3) | 100.59 (4) |
| $\gamma$, deg | 90 | 77.43 (3) | 66.45 (4) |
| $V$, Å$^3$ | 3117.8 | 1822.3 | 1837.8 |
| $Z$ | 8 | 4 | 4 |
| $\rho$(calcd), g/cm$^3$ | 1.680 | 1.572 | 1.566 |
| $\rho$(measd), g/cm$^3$ | 1.68 (2) | | 1.57 (2) |

the compound and that the interactions are sensitive to the nature of both the chalcogen and anion.[9,10] In addition, the structural features are also influenced by the organic groups and the presence or absence of solvent of crystallization.[9]

The dependence of the weak-bonding interactions on the nature of the chalcogen atom can be explained by the relative positions of the chalcogens in the periodic table. Tellurium, for example, with its expanded valence shell, shows higher coordination numbers than does selenium or sulfur, and it has the greatest propensity for secondary interaction. Tellurium is both five- and six-coordinate in the compound $(C_6H_5)_3TeNCS$,[6] whereas selenium in $(C_6H_5)_3SeNCS$ is only four-coordinate.[7] Accordingly, the former salt is oligomeric while the latter is monomeric.

The paucity of structural data on these compounds prevents similar generalizations to be made about the structural influence of the anion, the organic groups, and the solvent. We now report the first structural example of an $R_3TeX$ salt, in a series of salts, containing a monatomic anion, X. Previous determinations involved salts containing polyatomic anions such as the pseudohalides, tetraphenylborate, and $CH_3TeI_4^-$.[9] In addition, two solvated forms of $(C_6H_5)_3TeCl$ have been identified and their cell constants determined.

## Experimental Section

Triphenyltelluronium chloride was obtained from Organometallics Inc., East Hampstead, N.H. 03826. High-quality crystals for X-ray diffraction were obtained from a one-to-one volume mixture of methanol and absolute ethanol by open-air evaporation. The relative humidity was 68%. Elemental analysis and infrared spectra showed no solvent or water of crystallization.

Unit cell parameters were obtained by computer centering 25 reflections followed by least-squares refinement of the setting angles. The results are reported in Table I. The observed systematic extinctions were $h0l$, $h + l \neq 2n$, and $0k0$, $k \neq 2n$. The crystals were assigned to the monoclinic system of space group $P2_1/n$. Agreement of the observed (measured by flotation in $CCl_4$ and $Br_2CHCHBr_2$) and calculated densities was obtained for $Z = 8$.

Intensity data were collected at Molecular Structure Corp.[1] on an Enraf-Nonius CAD4 automatic diffractometer using graphite-monochromatized Mo K$\alpha$ radiation. The prism used was mounted on a glass fiber and measured 0.20 × 0.18 × 0.30 mm. The crystal orientation was random. The width at half-height from $\omega$ scans was 0.2°.

A total of 9722 independent reflections were collected by the $\theta$–$2\theta$ scan technique in the range $0 < 2\theta(\text{Mo K}\alpha) < 60°$. A takeoff angle of 2.8° was used with a counter aperture width of 2.0 mm. The incident-beam collimator diameter was 0.7 mm and the crystal to detector distance 21 cm. A variable scan rate of 4–40°/min (in $2\theta$) was used with moving-crystal–moving-counter background counts where scan time per background time equaled 2.0. The scan range was from $2\theta(\text{Mo K}\alpha_1) - 0.6°$ to $2\theta(\text{Mo K}\alpha_2) + 0.6°$.

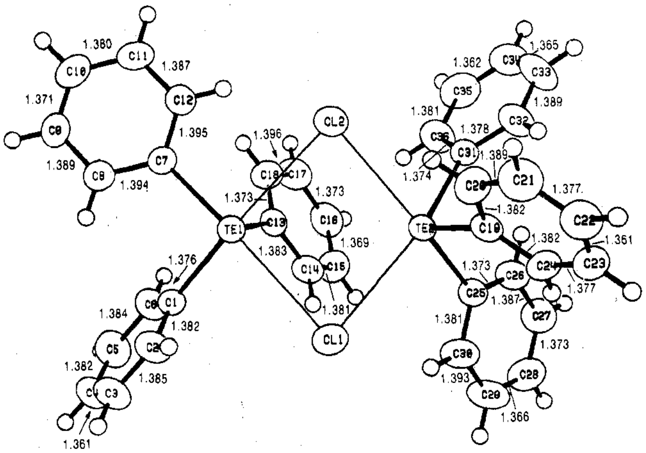


**Figure 1.** The $(C_6H_5)_3TeCl$ dimer, atom labeling scheme, and C–C distances (Å).

Intensities and standard deviations of intensities were calculated as described previously.[6] The factor $p$ was set to 0.05. No significant change was observed in the intensities of three check reflections measured periodically. Lorentz and polarization corrections were applied to the data. An absorption correction was applied by using the $\psi$ scan technique. The transmission factor varied a total of 5.1%. The calculated linear absorption coefficient, $\mu(\text{Mo K}\alpha)$, is 21.4 cm$^{-1}$.

The structure was solved by direct methods. A total of 16 phase sets were produced by using 397 reflections ($E_{\min} = 1.74$) and 2000 phase relationships. The two tellurium atoms were located from the $E$ map prepared from the phase set showing the best probability statistics (absolute figure of merit = 1.002; residual = 0.189). Least-squares refinement of the two Te atoms resulted in agreement factors of $R_1$ ($\sum||F_o| - |F_c||/\sum|F_o|$) = 0.28 and of $R_2$ ($[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$) = 0.32. The remaining nonhydrogen atoms were located in succeeding difference Fourier syntheses. The structure was refined anisotropically for nonhydrogen atoms and isotropically for hydrogen atoms.

Calculations were performed on a PDP 11/45 using the Enraf-Nonius structure determination package[12] and on a Xerox Sigma 9 system. Atomic scattering factors for all atoms were taken from the compilation of Cromer and Waber[13] and corrected for both the real and imaginary parts of anomalous dispersion.[14] In the full-matrix least-squares refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight $w$ is defined as $4F_o^2/\sigma^2(F_o^2)$. Only the 6719 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. Seventy atoms were determined by using 481 variable parameters. After the final complete cycles of refinement no parameter was found to shift by more than 0.1 of its estimated standard deviation. The estimated standard deviation of an observation of unit weight is 1.046. No unusual trends appeared in plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, $\lambda^{-1} \sin \theta$, reflection order in data collection, and various classes of indices. The final agreement factors (defined above) are $R_1 = 0.023$ and $R_2 = 0.031$. The final difference Fourier map showed no residual electron density as high as hydrogen atoms on a previous difference Fourier map.

The final positional and thermal parameters for the nonhydrogen atoms are given in Table II. The observed and calculated structure factors, the root-mean-square amplitudes of thermal vibration, and the positional and thermal parameters for hydrogen atoms are available as supplementary material.

---

(6) Lee, J.-S.; Titus, D. D.; Ziolo, R. F. *Inorg. Chem.* **1977**, *16*, 2487; *J. Chem. Soc., Chem. Commun.* **1976**, 501.

(7) Ash, P. A.; Lee, J.-S.; Titus, D. D.; Bowman, K.; Ziolo, R. F. *J. Organomet. Chem.* **1977**, *135*, 91.

(8) Mitcham, R. V.; Lee, B.; Mertes, K. B.; Ziolo, R. F. *Inorg. Chem.* **1979**, *18*, 3498.

(9) Ziolo, R. F.; Titus, D. D. Proceedings of the 3rd International Symposium on Organic Selenium and Tellurium Chemistry, Metz, France, July 9–12, 1979.

(10) In the absence of secondary interactions, simple ionic structures result.[11]

(11) Ziolo, R. F.; Troup, J. M. *Inorg. Chem.* **1979**, *18*, 2271–4.

(12) "Enraf-Nonius Structure Determination Package"; Enraf-Nonius: Delft, Holland, 1975; revised 1977 (Frenz and Okaya).

(13) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(14) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

**Table II.** Positional Parameters and General Temperature Factor Expressions for Atoms in $(C_6H_5)_3TeCl$[a, b]

| atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Te1 | 0.57690 (1) | 0.43771 (1) | 0.40793 (1) | 2.644 (5) | 2.412 (5) | 2.798 (5) | 0.118 (4) | 0.612 (4) | 0.053 (4) |
| Te2 | 0.51253 (1) | 0.55145 (1) | 0.22875 (1) | 2.380 (5) | 2.761 (5) | 2.712 (5) | −0.029 (4) | 0.351 (4) | 0.215 (4) |
| Cl1 | 0.75690 (6) | 0.57217 (5) | 0.34544 (3) | 3.59 (2) | 4.52 (3) | 3.78 (2) | −0.96 (2) | 1.08 (2) | −0.68 (2) |
| Cl2 | 0.33868 (6) | 0.55166 (5) | 0.32302 (3) | 3.11 (2) | 4.98 (3) | 4.12 (2) | 0.16 (2) | 0.70 (2) | 0.46 (2) |
| C1 | 0.7410 (2) | 0.3669 (2) | 0.4614 (1) | 2.54 (7) | 2.98 (8) | 3.01 (8) | 0.21 (7) | 0.67 (6) | 0.09 (7) |
| C7 | 0.4623 (2) | 0.3667 (2) | 0.4605 (1) | 2.96 (8) | 2.58 (8) | 2.99 (8) | −0.01 (7) | 0.82 (6) | 0.00 (7) |
| C13 | 0.5490 (2) | 0.3316 (2) | 0.3316 (1) | 2.93 (8) | 2.57 (7) | 2.81 (8) | 0.22 (7) | 0.32 (7) | 0.02 (7) |
| C19 | 0.4957 (2) | 0.7071 (2) | 0.2117 (1) | 2.58 (8) | 2.69 (8) | 3.36 (8) | −0.21 (7) | 0.20 (7) | −0.02 (7) |
| C25 | 0.6242 (2) | 0.5196 (2) | 0.1634 (1) | 3.03 (8) | 2.79 (8) | 3.15 (8) | 0.04 (7) | 0.76 (7) | −0.07 (7) |
| C31 | 0.3450 (2) | 0.5133 (2) | 0.1613 (1) | 2.45 (7) | 3.48 (9) | 2.95 (8) | −0.17 (7) | 0.39 (6) | −0.06 (7) |
| C2 | 0.8309 (2) | 0.4273 (2) | 0.4989 (1) | 3.5 (1) | 3.33 (9) | 4.5 (1) | −0.03 (8) | 0.16 (9) | −0.33 (9) |
| C3 | 0.9371 (3) | 0.3849 (2) | 0.5369 (1) | 3.6 (1) | 5.8 (1) | 4.5 (1) | −0.4 (1) | −0.4 (1) | −0.3 (1) |
| C4 | 0.9533 (2) | 0.2841 (2) | 0.5376 (1) | 3.3 (1) | 6.3 (1) | 4.5 (1) | 1.4 (1) | 0.37 (9) | 0.8 (1) |
| C5 | 0.8644 (3) | 0.2238 (2) | 0.4992 (1) | 5.0 (1) | 3.7 (1) | 5.5 (1) | 1.56 (9) | 0.8 (1) | 0.8 (1) |
| C6 | 0.7578 (2) | 0.2651 (2) | 0.4610 (1) | 3.6 (1) | 3.18 (9) | 4.4 (1) | 0.31 (8) | 0.42 (8) | −0.23 (9) |
| C8 | 0.5142 (2) | 0.3310 (2) | 0.5223 (1) | 3.39 (9) | 4.0 (1) | 3.17 (8) | 0.25 (8) | 0.91 (7) | 0.22 (8) |
| C9 | 0.4369 (2) | 0.2905 (2) | 0.5571 (1) | 4.9 (1) | 4.1 (1) | 3.41 (9) | 0.72 (9) | 1.65 (8) | 0.88 (8) |
| C10 | 0.3118 (2) | 0.2849 (2) | 0.5319 (1) | 4.6 (1) | 3.42 (9) | 4.7 (1) | −0.15 (9) | 2.40 (7) | −0.04 (9) |
| C11 | 0.2605 (2) | 0.3215 (2) | 0.4711 (1) | 2.97 (8) | 4.3 (1) | 5.0 (1) | −0.32 (8) | 1.41 (8) | −0.4 (1) |
| C12 | 0.3348 (2) | 0.3642 (2) | 0.4345 (1) | 3.23 (9) | 3.9 (1) | 3.68 (9) | 0.20 (8) | 0.71 (8) | 0.34 (9) |
| C14 | 0.6347 (2) | 0.3308 (2) | 0.2951 (1) | 2.97 (8) | 2.93 (8) | 4.03 (9) | 0.14 (7) | 0.80 (7) | −0.30 (8) |
| C15 | 0.6200 (2) | 0.2644 (2) | 0.2446 (1) | 4.4 (1) | 3.9 (1) | 4.1 (1) | 0.47 (9) | 1.57 (8) | −0.55 (9) |
| C16 | 0.5213 (3) | 0.2006 (2) | 0.2303 (1) | 5.1 (1) | 3.6 (1) | 3.9 (1) | 0.4 (1) | 0.56 (9) | −0.94 (9) |
| C17 | 0.4360 (3) | 0.2009 (2) | 0.2664 (1) | 4.2 (1) | 3.9 (1) | 4.7 (1) | −0.79 (9) | 0.3 (1) | −0.9 (1) |
| C18 | 0.4502 (2) | 0.2673 (2) | 0.3178 (1) | 3.61 (9) | 4.2 (1) | 3.9 (1) | −0.63 (9) | 1.14 (8) | −0.50 (9) |
| C20 | 0.4250 (2) | 0.7618 (2) | 0.2438 (1) | 4.4 (1) | 3.5 (1) | 4.2 (1) | −0.11 (9) | 1.57 (8) | −0.18 (9) |
| C21 | 0.4056 (3) | 0.8629 (2) | 0.2304 (2) | 5.5 (1) | 3.4 (1) | 6.1 (1) | 0.6 (1) | 1.7 (1) | −0.5 (1) |
| C22 | 0.4603 (3) | 0.9078 (2) | 0.1869 (2) | 4.5 (1) | 2.76 (9) | 6.7 (2) | −0.17 (9) | 0.8 (1) | 0.4 (1) |
| C23 | 0.5316 (2) | 0.8536 (2) | 0.1565 (1) | 3.9 (1) | 3.7 (1) | 6.0 (1) | −0.23 (9) | 1.34 (9) | 1.4 (1) |
| C24 | 0.5496 (2) | 0.7528 (2) | 0.1681 (1) | 3.28 (8) | 3.6 (1) | 4.6 (1) | 0.02 (8) | 1.45 (7) | 0.54 (9) |
| C26 | 0.5743 (2) | 0.4855 (2) | 0.1022 (1) | 3.50 (9) | 5.1 (1) | 3.6 (1) | −0.0 (1) | 0.64 (8) | −0.5 (1) |
| C27 | 0.6509 (3) | 0.4606 (2) | 0.0629 (1) | 4.8 (1) | 6.0 (1) | 3.5 (1) | 0.1 (1) | 1.20 (9) | −1.3 (1) |
| C28 | 0.7766 (3) | 0.4690 (2) | 0.0854 (1) | 4.4 (1) | 5.4 (1) | 4.7 (1) | 0.4 (1) | 2.16 (8) | −0.9 (1) |
| C29 | 0.8265 (2) | 0.5035 (3) | 0.1461 (1) | 3.0 (1) | 8.4 (2) | 5.3 (1) | 0.1 (1) | 1.24 (9) | −1.3 (1) |
| C30 | 0.7505 (2) | 0.5283 (2) | 0.1862 (1) | 3.00 (9) | 6.6 (1) | 4.0 (1) | −0.4 (1) | 0.90 (8) | −1.3 (1) |
| C32 | 0.2679 (3) | 0.5826 (2) | 0.1242 (1) | 3.8 (1) | 4.0 (1) | 4.3 (1) | 0.3 (1) | −0.4 (1) | −0.1 (1) |
| C33 | 0.1586 (3) | 0.5504 (3) | 0.0828 (2) | 4.2 (1) | 7.0 (2) | 4.6 (1) | 1.2 (1) | −1.2 (1) | −0.2 (1) |
| C34 | 0.1293 (3) | 0.4512 (3) | 0.0791 (1) | 3.4 (1) | 7.7 (2) | 4.4 (1) | −1.3 (1) | 0.0 (1) | −1.3 (1) |
| C35 | 0.2054 (3) | 0.3829 (2) | 0.1161 (2) | 4.8 (1) | 5.5 (1) | 5.7 (1) | −2.4 (1) | 0.7 (1) | −1.2 (1) |
| C36 | 0.3143 (3) | 0.4137 (2) | 0.1577 (1) | 4.2 (1) | 3.9 (1) | 4.9 (1) | −0.9 (1) | 0.2 (1) | 0.1 (1) |

[a] Values in parentheses in this and other tables are estimated standard deviations in the last significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$; the $B_{ij}$ are related to the dimensionless $\beta_{ij}$ employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$ for $i = j$ and as $2\beta_{ij}/a_i^*a_j^*$ for $i \neq j$.

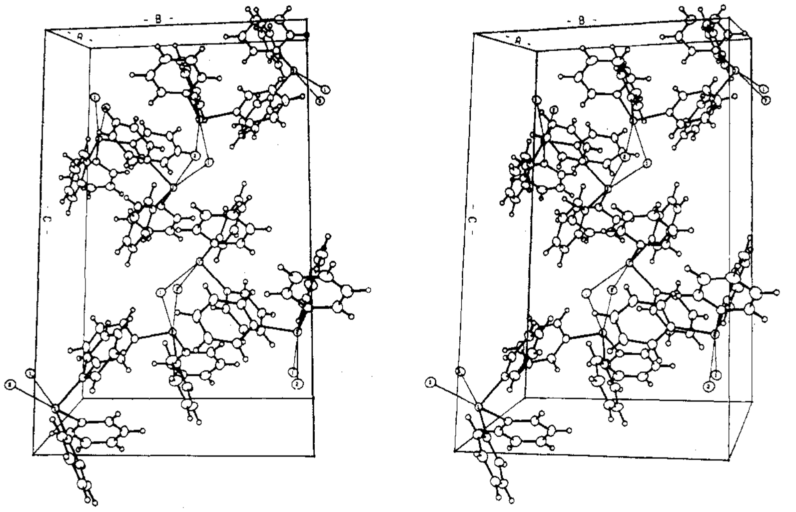


**Figure 2.** Stereoscopic unit cell view of $(C_6H_5)_3TeCl$.

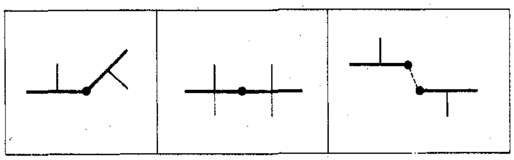
## Results and Discussion

Unsolvated triphenyltelluronium chloride is predominantly ionic in the solid state and is composed of noncentrosymmetric dimers separated by normal van der Waals distances. An illustration of the dimer and atom-labeling scheme is presented in Figure 1. Additional distances and angles are given in Table III, and a stereoscopic unit cell view is given in Figure 2.

Two chloride ions bridge the $(C_6H_5)_3Te^+$ ions with the Te–Cl distances ranging from 3.142 (1) to 3.234 (1) Å. These distances are comparable to the secondary Te–Cl distances in tetrameric $TeCl_4$, which average 2.929 Å[16] and are sig-

**Table III.** Interatomic Distances (Å) and Angles (Deg)

| | | | |
|---|---|---|---|
| | Distances | | |
| Te1–Te2 | 4.036 (0.5) | Te2–Cl1 | 3.227 (1) |
| Te1–Cl1 | 3.234 (1) | Te2–Cl2 | 3.142 (1) |
| Te1–Cl2 | 3.214 (1) | Te2–C19 | 2.115 (2) |
| Te1–C1 | 2.129 (2) | Te2–C25 | 2.144 (2) |
| Te1–C7 | 2.134 (2) | Te2–C31 | 2.125 (2) |
| Te1–C13 | 2.134 (2) | Cl1–Cl2 | 4.593 (1) |
| | Angles | | |
| Cl1–Te1–Cl2 | 90.84 (2) | Cl1–Te2–C19 | 94.10 (6) |
| Cl1–Te1–C1 | 85.90 (6) | Cl1–Te2–C25 | 90.39 (6) |
| Cl1–Te1–C7 | 171.00 (6) | Cl1–Te2–C31 | 169.15 (7) |
| Cl1–Te1–C13 | 92.11 (6) | Cl2–Te2–C19 | 93.90 (7) |
| Cl2–Te1–C1 | 176.73 (6) | Cl2–Te2–C25 | 168.45 (6) |
| Cl2–Te1–C7 | 89.38 (6) | Cl2–Te2–C31 | 81.80 (6) |
| Cl2–Te1–C13 | 86.45 (6) | C19–Te2–C25 | 97.12 (9) |
| C1–Te1–C7 | 93.88 (9) | C19–Te2–C31 | 95.36 (9) |
| C1–Te1–C13 | 93.38 (8) | C25–Te2–C31 | 93.69 (9) |
| C7–Te1–C13 | 96.88 (9) | Te1–Cl1–Te2 | 77.31 (1) |
| Cl1–Te2–Cl2 | 92.28 (2) | Te1–Cl2–Te2 | 78.82 (2) |



$(C_6H_5)_3TeCl$ $(C_6H_5)_3SeCl\cdot 2H_2O$ $(C_6H_5)_3TeNCS$

**Figure 3.** Idealized end-on schematic views of the chalcogenonium salt dimers.

nificantly less than the van der Waals distance of 3.8 Å.[17]

The two tellurium atoms are each five-coordinate and have a distorted square-pyramidal geometry. An examination of the C–Te–Cl angles in Table III shows that the distortions around Te1 are less severe than those about Te2. The largest angular deviation from the ideal value of 90° is 81.80 (6)° for C31–Te2–C2. Both tellurium atoms are essentially in the basal plane of their respective pyramids. The weighted least-squares planes are provided as supplementary material. Similar, but more distorted, geometries apper in the tetramers of $(C_6H_5)_3TeNCO$[4] and $(C_6H_5)_3TeNCS$[6] and in $((C_6H_5)_2TeNCS)_2O$.[15]

The $(C_6H_5)_3TeCl$ dimer is formed by the sharing of a common basal edge by the two square pyramids through the bridging chloride ions. The dimers are bent with the dihedral angle between the two pyramid bases being 128.8° and with the axial Te–C vectors pointing in opposing directions. The dihedral angle between the Te1Cl1Cl2–Te2Cl1Cl2 planes is 129.1°. The Te–Te and Cl–Cl core distances are 4.036 (0.5) and 4.593 (1) Å, respectively. The Cl–Te–Cl angles are 90.84 (2) and 92.28 (2)° while the Te–Cl–Te angles are 77.31 (1) and 78.82 (2)°.

The present chloride, $(C_6H_5)_3TeNCS$, which coexists with a tetramer,[6] and $(C_6H_5)_3SeCl\cdot 2H_2O$[5] consitute the three known triorganochalcogenonium salt dimers. All three differ morphologically and are compared schematically in Figure 3. In the six-coordinate selenium salt, the core is planar relative to that in the tellurium compounds, and the axial Se–C vectors point approximately in the same direction. The Se–Cl–Se and Cl–Se–Cl angles are larger than the corresponding angles in the tellurium salt. Distortions of the geometry in the selenium salt are very pronounced and make further comparisons difficult. Despite the larger size of the tellurium atom, both the Te–Te and Cl–Cl distances in the present compound are shorter than the corresponding distances in the selenium salt. These differences appear to be due, principally, to configurational differences between the salts.

The coordination around tellurium in the chloride compares more favorably with that in $(C_6H_5)_3TeNCS$. In the thiocyanate, however, the dimer is centrosymmetric with parallel basal planes and the axial Te–C vectors point in opposite directions. The configurational differences between the dimers must be attributed in part to differences in the bonding requirements of the bridging anions and to the packing requirements of the oligomers. That the latter might influence the oligomer configuration is evidenced by the fact that the coordination of the bridging ion in the step-type tetramer of $(C_6H_5)_3TeNCS$ is totally different from that in the dimer.[6]

The $(C_6H_5)_3Te^+$ ion has the expected trigonal-pyramidal shape. The C–Te–C angles fall at the low end of the range of C–Te–C angles found in other $(C_6H_5)_3Te^+$ salts consistent with the slightly more regular five coordinate geometry in the chloride. The six Te-C distances in the two cations are normal and have a mean value of 2.130 (4) Å.[19] The six phenyl rings are planar and have the random orientation typically found in other structures involving the $(C_6H_5)_3Te^+$ and $(C_6H_5)_3Se^+$ ions.[9] The dihedral angles between the phenyl rings range from 62 to 88°. The weighted least-squares planes of the phenyl rings are available as supplementary material. The two largest single carbon atom deviations from the plane are C12 at −0.017 Å and C7 at 0.012 Å.

The C–C distances in $(C_6H_5)_3TeCl$ are given in Figure 1 and have a mean value of 1.379 (2) Å. The mean value of the 36 C–C–C angles is 120.1 (1)°. The smallest angle is 118.7 (2) (C7–C8–C9) and the largest, 121.3 (3)° (C8–C9–C10). The C–H distances vary from 0.80 (3) to 1.04 (4) Å and have a mean value of 0.92 (1) Å. There are no unusually short Te–C contacts. The shortest intermolecular Te–C approach is Te1–C8 ($1-x$, $1-y$, $1-z$) at 3.692 (3) Å. This distance is comparable to the tellurium–aromatic carbon packing distances observed by McCullough.[20] The shortest intramolecular Te–C distance between the two independent cations is Te2–C14 at 3.412 (2) Å.

The effect of solvent on the structure of $(C_6H_5)_3TeCl$ is under investigation. Earlier evidence suggesting a critical role for solvent of crystallization in the structures of the $R_3MX$ salts was obtained from infrared data on $(C_6H_5)_3TeNCO\cdot {}^1/_2CHCl_3$ and its nonsolvated form.[3] Recently, the structure and chemistry of $(C_6H_5)_3SeCl$ were shown to be critically dependent on water of crystallization, and we note that only solvated forms of $(C_6H_5)_3SeCl$ have been characterized.[8] In contrast, $(C_6H_5)_3TeCl$ does not share this criticality with its selenium analogue nor does it show a particular propensity for water. We have identified, however, two solvated forms of $(C_6H_5)_3TeCl$ involving a polar and a nonpolar solvent.[18] Cell constants for $(C_6H_5)_3TeCl\cdot {}^1/_2(C_2H_5)_2O$ and $(C_6H_5)_3TeCl\cdot {}^1/_2C_6H_6$ are reported in Table I, and preliminary X-ray results indicate that the compounds are not dimeric. The results of these structural studies will be reported in subsequent publications.

**Registry No.** $(C_6H_5)_3TeCl$, 31426-14-9; $(C_6H_5)_3TeCl\cdot {}^1/_2(C_2H_5)_2O$, 74176-19-5; $(C_6H_5)_3TeCl\cdot {}^1/_2C_6H_6$, 74176-20-8.

**Supplementary Material Available:** Listings of observed and calculated structure factors, root-mean-square amplitudes of thermal vibration, positional and thermal parameters for the hydrogen atoms, and weighted least-squares planes (42 pages). Ordering information is given on any current masthead page.

---

(15) Mancinelli, C. S.; Titus, D. D.; Ziolo, R. F. *J. Organomet. Chem.* **1977**, *140*, 113.

(16) Buss, B.; Krebs, B. *Inorg. Chem.* **1971**, *10*, 2795.

(17) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

(18) Ziolo, R. F.; Smith, C. S.; Titus, D. D., to be submitted for publication.

(19) Estimated variances of the mean values of chemically equivalent distances or angles were calculated as $[\sum(x-\bar{x})^2/(n(n-1))]^{1/2}$.

(20) McCullough, J. D.; Knobler, C. *Inorg. Chem.* **1976**, *15*, 2728 and references therein.