

The Crystal Structure of Tetrakis(ethylenethiourea)-tellurium(II) Hexachlorotellurate(IV)

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Crystals of tetrakis(ethylenethiourea)tellurium(II) hexachlorotellurate(IV), $[\text{Te}(\text{etu})_4][\text{TeCl}_6]$, are orthorhombic, space group, $C222_1$, with cell dimensions $a = 12.0687(4) \text{ \AA}$, $b = 15.8058(6) \text{ \AA}$, $c = 15.0231(5) \text{ \AA}$. There are four formula units in the cell. Reflection intensities were collected on a diffractometer and the structure was solved and refined by conventional X-ray crystallographic methods to an R value of 0.056. The structure is built up of $[\text{Te}(\text{etu})_4]^{2+}$ cations and $[\text{TeCl}_6]^{2-}$ anions stacked in chains along a . The coordination around the central tellurium atoms are square planar and octahedral for the cations and the anions, respectively. The average Te(II)–S bond length is 2.681 Å, whereas the average Te(VI)–Cl bond length is 2.530 Å.

The solution of the structure of the complex salt, $[\text{TeC}_3\text{H}_6\text{N}_2\text{S}_4]^{2+}[\text{TeCl}_6]^{2-}$, was undertaken as a part of a study of the stereochemical activity of the unshared electron pair in highly coordinated complexes of tellurium(IV). Tellurium(IV) has an electron configuration of $4d^{10}5s^2$. Thus, according to the valence shell electron pair repulsion theory (VSEPR),^{1,2} a hexacoordinate tellurium(IV) complex should have a lone pair of electrons occupying the seventh position of a pentagonal bipyramid, or situated above one of the rectangular faces of a trigonal prism, or above one of the faces of an octahedron such that great distortion from octahedral symmetry occurs. It has been found, however, that several ions in the lower right-hand corner of the periodic table with electron configurations $(n-1)d^{10}ns^2$ form complexes with stereochemically inert lone pairs.^{3–5} This has been found true for several octahedral and dodecahedral complexes of tellurium(IV).^{6–9} This effect has been explained as being caused by delocalization of the lone pair on the ligands,^{10,11} a three-center four-

electron bond system,¹² or steric effects.^{2,13} Mössbauer studies indicate the presence of three-center four-electron bonding in octahedral tellurium(IV) complexes.¹⁴ Recently it has been indicated that the lone pair may become stereochemically active in such complexes.¹⁵ The structure of TeCl_6^{2-} has been previously determined with small cations.^{16,17} The present investigation was partly undertaken in order to determine whether the influence of a larger cation will affect the stereochemical activity of the lone pair.

EXPERIMENTAL

The preparation of tetrakis(ethylenethiourea)-tellurium(II) hexachlorotellurate(IV) has been previously reported.¹⁸ The crystals are orthorhombic with $a = 12.0687(4) \text{ \AA}$, $b = 15.8058(7) \text{ \AA}$, and $c = 15.0231(5) \text{ \AA}$. There are four formula units per cell. Calculated and observed densities are 2.03 and 2.01 g/cm³, respectively.

The crystal chosen for data collection was mounted along the prism axis, a . It had a length of 0.25 mm and its cross section was $0.12 \times 0.12 \text{ mm}^2$. Weissenberg photographs showed systematic extinctions of reflections hkl when $h+k=2n+1$, and of $00l$ when $l=2n+1$, corresponding to space group $C222_1$. This space group has eight general positions, therefore the tellurium atoms must be located in special positions on two-fold axes. Reflections hkl also appear to be systematically weak when $h=2n+1$ or $k=2n+1$.

A Siemens papertape-controlled single crystal diffractometer (AED-1) was used for data collection. The diffractometer was operated as a three-circle instrument using $\text{MoK}\alpha$ radiation. The intensities of 2326 independent reflections with $\theta \leq 30^\circ$ were measured using a scintillation counter, the "five-value" measurement, and $\theta-2\theta$ scan¹⁹ at a speed

of 2.5°/min with automatic setting of greater speed for strong reflections. To reduce counting losses, attenuation filters were automatically inserted in the beam. The reflections were scanned between $\theta_1 = \theta - 0.32$ and $\theta_2 = \theta + 0.32 + 0.35 \tan \theta$ (units are degrees), where θ is the Bragg angle for the α_1 peak. Three reference reflections were measured twice each at intervals of fifty reflections and used to scale the intensities of the recorded reflections. The intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 26.5 \text{ cm}^{-1}$). Of the reflections measured, 279 had intensities less than twice the standard deviation in net intensities and were regarded as unobserved. Cell dimensions were determined by means of a least-squares procedure based on accurate measurements of the Bragg angle for the α_1 peak of 20 high order reflections ($\theta > 20^\circ$).

STRUCTURE ANALYSIS

The Patterson map gave the position of one tellurium atom on the twofold axis $0, y, 1/4$, and the other on the twofold axis $1/2, y, 1/4$ in the asymmetric unit. The asymmetric unit thus contains two half tellurium atoms, one from the anion and one from the cation, and both were found to have $y \approx 1/8$. This is also consistent with the observed pseudo-extinctions. A Fourier map based on these tellurium positions was then calculated. Tentative positions for the chlorine and sulfur atoms were then found, but they were heavily obscured because of false mirror planes resulting from the special y -coordinates for the tellurium atoms in the special positions above. After refinement of the possible trial structures, the correct structure emerged.

The structure was then further refined by means of full matrix least squares procedures. The computer programs used in this investigation are those of the X-ray system, version of 1972.²⁰ The weights used in the refinement were set equal to $1/\sigma(F_{\text{rel}})$ squared.

After the hydrogen atoms had been found, the conventional R -factor¹² converged to the final value of 0.056. In the presence of the heavy atoms the hydrogen parameters did not refine well. The hydrogen atoms were therefore held fixed at positions found from a difference map and use of a molecular model. Likewise the U values for these atoms were held constant and set equal to 0.044. Further refinement of the enantiomorphous structure demonstrated that the correct structure had been chosen.²¹

A final difference map revealed peaks of about $7e/\text{\AA}^3$ located near the tellurium atoms, indicating that these atoms should be moved such that their y -coordinates would have values closer to $1/8$. Because of their positions at $y \approx 1/8$ the tellurium atoms contribute mostly to the structure factors of the strong reflections which are given low weight. A new weighting scheme which gives unit weight to all reflections was then introduced. Thus, the reflections to which tellurium contributes most, were given greater weight. The new weighting scheme resulted in a shift in the positions of both tellurium atoms less than 0.0001 \AA towards $y = 1/8$ and only a small decrease in the height of the spurious peaks in the difference map. As a result of this refinement, the tellurium-ligand bond lengths changed less than one standard deviation. As this new refinement was also accompanied by an

Table 1. Atomic coordinates for atoms in the asymmetric unit in fractions of cell edges. Standard deviations are in parentheses.

	x	y	z
Te1	0	0.11624(6)	0.2500
Te2	0.5000	0.11060(6)	0.2500
Cl1	0.5000	0.2702(3)	0.2500
Cl2	0.5000	-0.0481(2)	0.2500
Cl3	0.3038(3)	0.1110(3)	0.1877(2)
Cl4	0.4134(3)	0.1089(3)	0.4035(2)
S1	0.0368(3)	0.2322(2)	0.1182(2)
S2	0.0411(2)	0.0010(2)	0.1284(2)
C1	-0.0875(10)	0.2840(7)	0.1098(8)
C2	-0.2096(11)	0.3854(9)	0.0619(10)
C3	-0.2705(12)	0.3278(9)	0.1261(11)
C4	-0.0841(9)	-0.0519(7)	0.1122(7)
C5	-0.2636(11)	-0.0937(9)	0.1183(11)
C6	-0.1957(11)	-0.1547(9)	0.0619(11)
N1	-0.1044(9)	0.3454(7)	0.0497(7)
N2	-0.1764(9)	0.2701(7)	0.1559(7)
N3	-0.1768(9)	-0.0371(7)	0.1502(8)
N4	-0.0911(8)	-0.1155(6)	0.0566(7)
H1	-0.024	0.355	0.025
H2	-0.172	0.432	0.072
H3	-0.262	0.389	0.010
H4	-0.260	0.355	0.180
H5	-0.353	0.293	0.123
H6	-0.201	0.195	0.192
H7	-0.202	0.023	0.161
H8	-0.310	-0.058	0.091
H9	-0.276	-0.122	0.151
H10	-0.206	-0.182	-0.001
H11	-0.184	-0.210	0.097
H12	-0.035	-0.152	0.034

Table 2. Components of atomic vibration tensors, $U \times 10^4$, in \AA^2 , with standard deviations, referred to crystallographic axes. The expression is $\exp\{-2\pi^2(h^2a^{-2}U_{11} + k^2b^{-2}U_{22} + l^2c^{-2}U_{33} + 2hka^{-1}b^{-1}U_{12} + 2klb^{-1}c^{-1}U_{23} + 2hla^{-1}c^{-1}U_{13})\}$

	$\begin{matrix} (U_{11}, \\ U_{12}, \end{matrix}$	$\begin{matrix} U_{22}, \\ U_{23} \end{matrix}$	$\begin{matrix} U_{33} \\ U_{13} \end{matrix}$
Te1	206(4) 0	319(4) 0	278(5) -9(4)
Te2	212(4) 0	427(5) 0	235(4) 53(4)
Cl1	734(34) 0	383(20) 0	806(34) 281(40)
Cl2	707(32) 0	378(18) 0	665(29) 191(38)
Cl3	316(15) 0(18)	880(25) 15(21)	565(18) -80(15)
Cl4	535(17) -132(19)	829(23) -82(17)	325(14) 118(14)
S1	315(14) -21(11)	365(14) 87(13)	443(16) 37(13)
S2	330(13) 3(13)	359(13) -76(13)	415(16) 37(14)
C1	430(57) -22(47)	307(53) -46(46)	300(59) -3(54)
C2	464(76) 130(67)	436(70) 104(75)	610(82) 55(64)
C3	686(89) 239(74)	624(83) 148(76)	440(89) 120(78)
C4	325(50) 29(44)	333(52) -11(45)	284(57) -56(49)
C5	539(70) -93(73)	632(103) -184(83)	472(98) 8(75)
C6	371(66) 69(63)	456(78) -278(75)	761(97) -97(68)
N1	478(58) 71(51)	462(60) 199(52)	516(62) 98(53)
N2	323(57) 63(50)	491(61) 94(51)	480(63) 92(52)
N3	264(52) -5(48)	549(62) -284(58)	599(75) 51(55)
N4	458(53) -51(50)	306(47) -143(50)	479(54) 38(48)

The isotropic vibration tensor for the hydrogen atoms is fixed at $44 \times 10^{-3} \text{\AA}^2$, where the expression used is $\exp\{-8\pi^2U(\sin^2\theta/\lambda^2)\}$.

increase in the standard deviations of the atomic parameters, and only a slight reduction of the R -value, it was abandoned in favour of the former scheme.

Atomic scattering factors were taken from the *International Tables*.²² Those for tellurium, sulfur,

Table 3. Bond lengths in \AA , with standard deviations.

Cation		Anion	
Te1-S1	2.735(3)	Te2-Cl1	2.520(4)
Te1-S2	2.627(3)	Te2-Cl2	2.508(4)
S1-C1	1.714(12)	Te2-Cl3	2.546(3)
S2-C4	1.744(11)	Te2-Cl4	2.531(3)
C1-N1	1.34(2)		
C1-N2	1.30(2)		
C4-N3	1.28(2)		
C4-N4	1.31(1)		
C2-C3	1.52(2)		
C5-C6	1.51(2)		
C2-N1	1.43(2)		
C3-N2	1.52(2)		
C5-N3	1.46(2)		
C6-N4	1.41(2)		

and chlorine were corrected for anomalous dispersion.²⁰ Final atomic parameters are given in Tables 1 and 2. Interatomic distances and angles are listed in Tables 3 and 4. The structure factor table can be obtained from the author St. H. upon request.

DISCUSSION

The structure of the complex salt is shown in Fig. 1. The configuration around Te(II) (Te1 in the

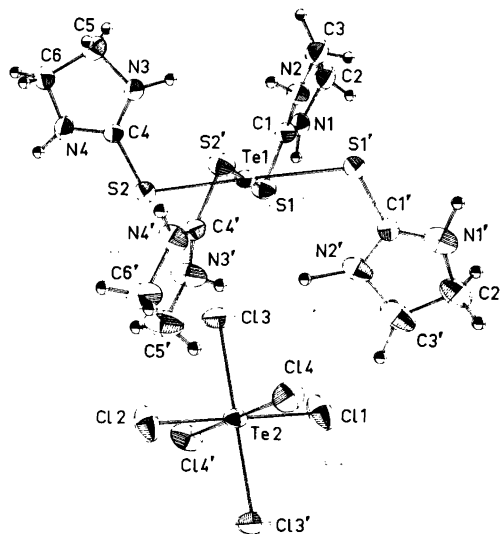


Fig. 1. The complex as seen along the original c direction after rotating the cell thirty degrees around a . Unprimed letters denote atoms in the symmetry related halves of the two complex ions.

Table 4. Bond angles in degrees, with standard deviations. Atoms related to those in the asymmetric unit by twofold symmetry axes are marked by primes.

Cation		Anion	
S1-Te1-S2	86.00(9)	Cl1-Te2-Cl2	180.00
S1-Te1-S1'	95.86(10)	Cl1-Te2-Cl3	89.85(10)
S1-Te1-S2'	177.40(9)	Cl1-Te2-Cl4	90.60(9)
S2-Te1-S2'	92.21(10)	Cl2-Te2-Cl3	90.15(10)
Te1-S1-C1	103.4(4)	Cl2-Te2-Cl4	89.40(9)
Te1-S2-C4	105.4(4)	Cl3-Te2-Cl4	87.18(11)
S1-C1-N1	121.9(9)	Cl3'-Te2-Cl4	92.82(11)
S1-C1-N2	127.2(9)	Cl3-Te2-Cl3'	179.70(13)
N1-C1-N2	110.9(10)	Cl4-Te2-Cl4'	178.80(14)
C1-N1-C2	111.7(11)		
N1-C2-C3	104.2(11)		
C2-C3-N2	100.7(11)		
C3-N2-C1	111.0(11)		
S2-C4-N3	127.5(9)		
S2-C4-N4	120.8(8)		
N3-C4-N4	111.6(10)		
C4-N3-C5	111.7(11)		
N3-C5-C6	100.7(11)		
C5-C6-N4	103.6(11)		
C6-N4-C4	111.1(10)		

cation) is approximately square planar with an average Te-S bond length of 2.682(4) Å, which is in agreement with those found previously for square planar complexes of Te(II) with sulfur-containing ligands.²³ This is much larger than 2.41 Å, the sum of the covalent radii of tellurium and sulfur, indicating the presence of a linear three-center four-electron bonding system based on overlap of the *p*-orbitals of tellurium and sulfur. It has indeed been shown from Mössbauer studies that only the *p*-orbitals of the tellurium atom contribute to the bonding in such complexes.¹⁴ Here the system is very nearly linear, as can be seen from the S1-Te1-S2' bond angle of 177.40(9)°. As can be seen from Table 3 there is a significant difference in the lengths of the two Te-S bonds.

The ethylenethiourea rings are nearly planar with deviations in atomic positions of 0.01–0.07 Å from the plane. Average S-C bond lengths are 1.73 Å and C-N partial double bonds are 1.31 Å. C-N and C-C single bonds average 1.46 and 1.52 Å, respectively. These values are normal for ethylenethiourea ligands.^{23,24} The angles on the nitrogen atoms and C1 and C4 atoms correspond to *sp*² hybridization. The average C-H and N-H bond lengths are 0.95 and 1.09 Å, respectively. The angles on the ethylene carbons correspond to *sp*³ hybridization.

The configuration around Te(IV) (Te2 in the anion) is octahedral, in agreement with previous investigations.^{6,16} The Te-Cl bond lengths range from 2.508 Å to 2.546 Å with an average value of 2.533 Å. This is close to values around 2.54 Å which has been found previously in octahedral complexes of tellurium(IV).^{6,16} Again the bonding probably is of the three-center four-electron type.^{14,25,26} The Cl3-Te2-Cl4 angle and the interplanar angle Te2Cl1Cl3/Te2Cl1Cl4 are both close to 87°, which differs somewhat from the 90° expected with ideal octahedral coordination. This is probably due to a weak interaction between Cl3 and Te1 (of the cation), and will be discussed later. The seventh valency electron pair on tellurium appears again to be stereochemically inert.

The packing of the complex ions is shown in Fig. 2. There is an interaction between Te1 (of the cation) and Cl3 of two neighbouring anions, one of each side of the cation along the *a* axis with a Te-Cl distance of 3.785(3) Å, such that divalent tellurium tends toward octahedral coordination. This appears to be a very weak interaction, only 0.22 Å shorter than the sum of the van der Waals radii of Te and Cl, and it does not appear to significantly lengthen the Te2-Cl3 bond. It may, however, distort the octahedral coordination of the tetravalent tellurium atom, by decreasing the Cl3-Te2-Cl4 bond angle.

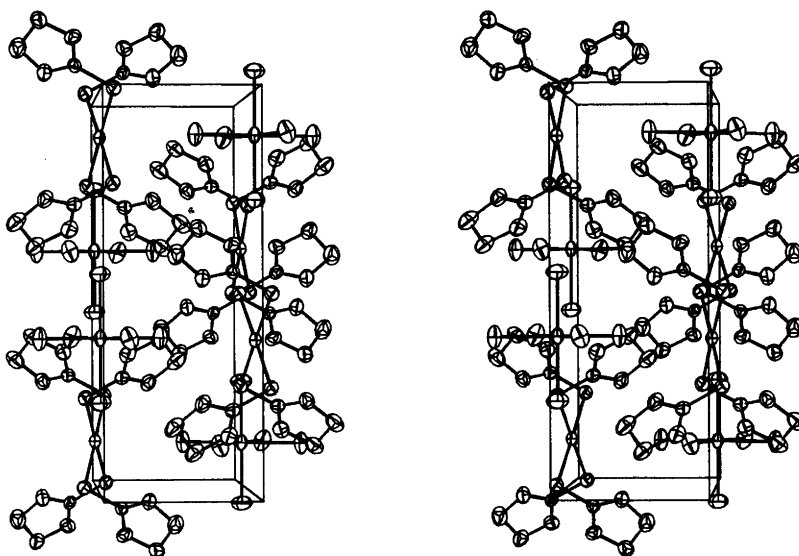


Fig. 2. A stereo view of the complex salt as seen along c . One half of a unit cell is outlined with $a/2$ being horizontal and b vertical. Hydrogen atoms are omitted.

The $\text{Te1}-\text{Cl3}-\text{Te2}$ angle is $144.12(9)^\circ$. Thus the anions and cations are stacked in zigzag chains parallel with the a -axis. The chain containing the asymmetric unit is shown in Fig. 3. All tellurium atoms in this chain of alternating octahedral anions and square planar cations containing tetravalent and divalent tellurium central atoms, respectively, have y coordinates close to $1/8$ and z coordinates equal to $1/4$. The x coordinates are $0, \pm \frac{1}{2}, \pm 1$ etc. starting with a cation. This stacking system, as expected, resembles similar ones found for $\text{Pt(II)}/\text{Pt(IV)}$ complexes with the same coordination.²⁷

The stereochemistry of tellurium resembles that of palladium and platinum. In the divalent state, square planar complexes predominate, whereas in the tetravalent state, octahedral complexes are often found. Zero-valent complexes of palladium and platinum have been known for some time, and recently a tellurium(0) complex has been found.²⁸ *trans*-Effects are also well known for all three elements,^{23,29,30} and they are all soft acids with large radii.

For palladium and platinum, complexes of the type $[\text{M(II)L}_4][\text{M(II)X}_4]$ and $[\text{M(II)L}_2\text{X}_2][\text{M(IV)L}_2\text{X}_4]$ with chain structures are well known.²⁷ Here L is a neutral ligand like NH_3 and X is a uninegative ligand, often a halogen ion. Complexes of the first

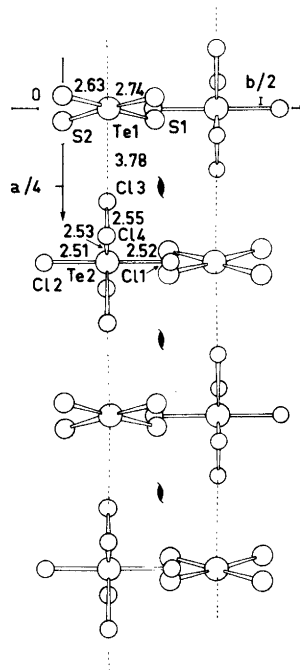


Fig. 3. Two neighbour anion-cation chains seen along c , with $\text{Te1}\cdots\text{Cl3}$ interactions indicated as dotted lines. Bond lengths (in Å) in the asymmetric unit are indicated, and the lighter atoms are omitted for clarity.

type are salts and are stacked in chains held together by M(II)···M(II) interactions. The ionic planes in alternating anions and cations are parallel. Complexes of the second type are held together by ···M(II)···X—M(IV)—X···M(II)··· interactions. Here the molecular plane of the M(II) complex is normal to the ···X—M(IV) bond.

Neighbour chains (Fig. 3) are related by two-fold screw axes parallel to *c*, so that the tellurium atoms in neighbour chains are $\frac{1}{2}$ above or below the original ones in the *z* direction. Also the tellurium atoms of the anions in the original chain have the same *x*-coordinate as the tellurium atoms in the cations in the neighbour chains and *vice versa*. Thus interactions between chains take place primarily between anions and cations. There are hydrogen bonds³¹ Cl4···H1—N1 with Cl4···H1 = 2.33(15) Å, Cl4···N1 = 3.26(1) Å and \angle Cl4···H1—N1 = 148(9)° holding neighbouring chains together.

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