Acta Chim. Slov. **2000**, *47*, 89–98.

THE NOVEL ROUTE FOR SYNTHESIS OF TELLURIUM TETRACHLORIDE, AND REDETERMINATION OF ITS STRUCTURE AT LOWER TEMPERATURE BY X-RAY CRYSTALLOGRAPHY.

Abdolali Alemi,[a] Esmaiel Soleimani,*[a] Zoya A. Starikova[b]

a : Inorganic Synthesis Laboratory, Faculty of Chemistry, Tabriz University, Tabriz, IRAN   Phone : 0098 41 355998, Fax : 0098 41 340191, soleimani@ark.tabrizu.ac.ir

b : X-ray Structural Center, General and Technical Chemistry Division, Academy of Science of Russia, star@xrpent.ineos.ac.ru

Received 1.12.1999

Abstract

The reaction of iodine trichloride with tellurium in a sealed evacuated glass ampoule at 250 °C yields yellow-green, moisture sensitive crystals of $TeCl_4$. The crystal structure of $TeCl_4$ has been determined in low temperature at 100 K from three-dimensional X-ray data collection. The compound crystallizes in space group *C2/c* of monoclinic system with unit cell dimensions a = 16.846(3)Å, b = 10.347(2)Å, c = 15.051(3) Å, β = 116.87(3) °, Z = 8, V = 2340.2(8) $Å^3$, ρ_c = 3.059 g/cm^3 , final *R* indices [$I>2\sigma (I)$] *R* = 0.0507, *wR* = 0.1304 , and *R* indices (all data) *R* = 0.0564, *wR* = 0.1341.

The structure consists of tetramers, Te_4Cl_{16}, which have a cubane-like structure. The Te atoms occupy the half of the corners with T_d symmetry. Each Te atom has been attached to three terminal Cl atoms with an average distance of 2.325Å. The coordination of the Te atom is completed to a distorted octahedron by three bridging chlorine atoms with much longer Te-Cl bond lengths (average 2.915Å). In the polar limiting case the structure may be described, in a rough approximation, as an arrangement of $TeCl_3^+$ ions with nearly C_{3v} symmetry and of Cl^- ions. The structure data suggest possible concentration of the nonbonding Te electrons toward the center of the cubane skeleton.

Introduction

The compounds R_3EX_2 (R = alkyl, aryl, mixed arylalkyl, substituted aryl ; E = P, As, Sb; X = Cl, Br, I) and R_2FX_2 (R = alkyl, aryl, mixed arylalkyl, substituted aryl ; F = S, Se ; X_2 = Cl_2, Br_2, I_2, ICl, IBr) are a subject of considerable current interest [1-6] . They were found significant use as reagent in synthetic organic and inorganic chemistry [7-11] . Recently structural study of these compounds were interested some of the chemists [12-16] .The dihalogen adducts of tertiary phoshphines [17,18] , arsines [2] , tertiary phosphine sulfides [15,19] , selenides [13, 20] , organo-selenium compounds [6, 21] and selenoamides [22-24] have all received considerable study from a variety of research groups in the last few years. It is surprising that many of the dihalogen compounds formed lie close the ionic and covalent borderline are influenced not only by aggregation (solid, liquid, gas) or the nature of solvent, but also by effect of organo-substituents , R , the donor atoms, the indentity of the halogen.

Thus, for example, dimethylselenide diiodine adopts a three coordinate charge transfer (CT) structure, Me_2Se-I-I [6] whereas the corresponding dibromide adopts a disphenoidal structure, Me_2SeBr_2 [6] . On the other hand, Me_2SBr_2 is a charge transfer compelex, Me_2S-Br-Br [25] , thus illustrating the importance of the donor atom on the nature of the dihalogen adduct produced. Similarly Ph_3As-I-I [2] is a charge transfer complex, whereas Ph_3AsBr_2 [2] is trigonal bipyramidal.

Recently, we have prepared adduct Cl_2Se-ICl [26] from the reaction of Se and ICl_3 in a sealed evacuated ampoule. In an analogous attempt to synthesis adduct Cl_2Te-ICl from the reaction of Te and ICl_3, we have obtained yellow-green crystals of $TeCl_4$ by chemical vapour transport reaction.

Experimental

Iodine trichlorid (ICl_3) was prepared by interaction finely powdered iodine crystals and potassium chlorate ($KClO_3$) with together addition gradually dropwise concentrated HCl. Then it was recrystallized in absolute ethanol, and dried over $CaCl_2$ in vacuum. Tellurium was used as purchased.

Preparation of $TeCl_4$

0.2300 g Te and 0.6130 g ICl_3 are filled in a glass ampoule of 25 cm length and 1.5 cm inner diameter. The glass ampoule was evacuated and simultaneously heated with burner flame. The ampoule is placed in a horizontal tube furnace in a temperature gradient from 250 °C to 100 °C with the educt mixture at the hot side. Within three days yellow-green crystals of $TeCl_4$ were transported into the colder part of the ampoule. The yield was nearly quantitative.

Due to the high sensitivity towards moist air charging and opening of the reaction ampoule and collection of crystals were performed in the glove box filled with argon atmosphere.

Crystal Structure Analysis

The single crystal of $TeCl_4$ with size 0.1 x 0.1 x 0.2 mm was fixed to glass capillary tube, which was closed by flame for X-ray diffraction study. Intensity data were collected at 100 °K on a Rigaku AFC7R diffractometer. Preliminary precession photographs showed the monoclinic crystal system with the Laue group *2/m* and the centered unit cell. The systematic extinction *hol* only present for $l = 2n$ was confirmed in the diffractometer data set and led to the space groups *C2/c* or *Cc*. The centrosymmetry of the structure with the space group *C2/c* was confirmed through the structure analysis. 13755 reflections collected with 2θ range for data collection 4.78 ° to 60.16 °.A structure mode was obtained by direct method and refined by full matrix least square on F^2 with anisotropic displacement parameters for all atoms. The maximum and minimum peaks on the final difference Fourier map corresponded to 4.262 and -3.507 $eÅ^{-3}$.

Crystallographic data and details of structure analysis are given in Table 1. Table 2 contains the atomic coordinates and equivalent isotropic displacement parameters. Bond lengths and angles are given in Table 3. Table 4 contains the anisotropic displacement parameters.

Details of the crystal structure determination can be ordered from FACHINFORMATIONSZENTRUM KARLSRUHE, 76344 Eggenstein-Leopoldshafen, under the depository number CSD-411157.

Table 1. Crystal data and structure refinement for $TeCl_4$.

Identification code	$TeCl_4$
Empirical formula	Cl_8Te_2
Formula weight	538.80
Temperature	100(1) °K
Wavelength	0.7103 Å
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions	a = 16.846(3) Å, $\alpha = 90^{o}$
	b = 10.347(2) Å, $\beta = 116.87(3)^{o}$
	c = 15.051(3) Å, $\gamma = 90^{o}$
Z	8
Volume	2340.2(8) $Å^3$
Calculated density	3.059 Mgm^{-3}
Absorption coefficient	6.750 mm^{-1}
F(000)	1920
Crystal size	0.1 x 0.1 x 0.2 mm
θ range for data collection	2.39° to 30.08°
Limiting indices	$-23 \leq h \leq 23$, $-14 \leq k \leq 14$, $-21 \leq l \leq 21$
Reflections collected	13755
Independent reflections	3395 (R_{int} = 0.0831)
Completeness to data	up to θ =30.08° 98.9 %
Max. and Min. transmission	1.258 and 0.352
Refinement method	Full-matrix least-squares on F^2
Data /restraints /parameters	3395 / 0 / 91
Goodness-of-fit on F^2	1.009
Final *R* indices [$I>2\sigma(I)$]	*R* = 0.0507, *wR* = 0.1304
R indices (all data)	*R* = 0.0564, *wR* = 0.1341
Largest diff. peak and hole	4.262 and -3.507 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for $TeCl_4$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	**X**	**Y**	**Z**	**U_{eq}**
Te(1)	3571(1)	5248(1)	1797(1)	14(1)
Te(2)	5019(1)	2317(1)	3918(1)	14(1)
Cl(1)	5003(1)	5124(1)	3801(1)	18(1)
Cl(2)	3647(1)	2443(1)	1821(1)	19(1)
Cl(3)	2526(1)	5208(2)	129(1)	23(1)
Cl(4)	2547(1)	5117(2)	2434(1)	23(1)
Cl(5)	3661(1)	7498(1)	1878(1)	25(1)
Cl(6)	6176(1)	2377(1)	5520(1)	21(1)
Cl(7)	3901(1)	2401(1)	4414(1)	20(1)
Cl(8)	5003(1)	77(1)	3770(1)	21(1)

Table 3. Bond lengths [Å] and angles [°] for $TeCl_4$.

Te(1)-Cl(4)	2.324(2)	Te(1)-Cl(3)	2.325(2)
Te(1)-Cl(5)	2.333(2)	Te(1)-Cl(1)	2.891(2)
Te(1)-Cl(2)	2.905(2)	Te(1)-Cl(1)#1	2.925(2)
Te(2)-Cl(6)	2.317(2)	Te(2)-Cl(7)	2.320(2)
Te(2)-Cl(8)	2.328(2)	Te(2)-Cl(1)	2.910(2)
Te(2)-Cl(2)#1	2.928(2)	Te(2)-Cl(2)	2.954(2)
Cl(1)-Te(1)#1	2.925(2)	Cl(2)-Te(2)#1	2.928(2)
Cl(4)-Te(1)-Cl(3)	95.95(6)	Cl(4)-Te(1)-Cl(5)	94.55(6)
Cl(3)-Te(1)-Cl(5)	94.22(6)	Cl(4)-Te(1)-Cl(1)	89.55(5)
Cl(3)-Te(1)-Cl(1)	173.28(6)	Cl(5)-Te(1)-Cl(1)	89.19(5)
Cl(4)-Te(1)-Cl(2)	88.46(5)	Cl(3)-Te(1)-Cl(2)	90.18(5)
Cl(5)-Te(1)-Cl(2)	174.38(5)	Cl(1)-Te(1)-Cl(2)	86.08(4)
Cl(4)-Te(1)-Cl(1)#1	171.87(5)	Cl(3)-Te(1)-Cl(1)#1	89.59(5)
Cl(5)-Te(1)-Cl(1)#1	90.96(5)	Cl(1)-Te(1)-Cl(1)#1	84.55(5)
Cl(2)-Te(1)-Cl(1)#1	85.56(4)	Cl(6)-Te(2)-Cl(7)	95.01(6)
Cl(6)-Te(2)-Cl(8)	95.39(5)	Cl(7)-Te(2)-Cl(8)	95.28(5)
Cl(6)-Te(2)-Cl(1)	90.95(5)	Cl(7)-Te(2)-Cl(1)	89.75(4)
Cl(8)-Te(2)-Cl(1)	171.53(5)	Cl(6)-Te(2)-Cl(2)#1	87.99(5)
Cl(7)-Te(2)-Cl(2)#1	174.37(5)	Cl(8)-Te(2)-Cl(2)#1	89.17(5)
Cl(1)-Te(2)-Cl(2)#1	85.43(4)	Cl(6)-Te(2)-Cl(2)	174.08(5)
Cl(7)-Te(2)-Cl(2)	89.15(5)	Cl(8)-Te(2)-Cl(2)	88.40(5)
Cl(1)-Te(2)-Cl(2)	84.85(4)	Cl(2)#1-Te(2)-Cl(2)	87.52(5)
Te(1)-Cl(1)-Te(2)	95.03(4)	Te(1)-Cl(1)-Te(1)#1	95.23(5)
Te(2)-Cl(1)-Te(1)#1	94.35(4)	Te(1)-Cl(1)-Cl(1)#2	131.75(7)
Te(2)-Cl(1)-Cl(1)#2	82.71(5)	Te(1)#1-Cl(1)-Cl(1)#2	133.02(5)
Te(1)-Cl(2)-Te(2)#1	94.39(4)	Te(1)-Cl(2)-Te(2)	93.78(4)
Te(2)#1-Cl(2)-Te(2)	92.25(5)		

Symmetry transformations used to generate equivalent atoms: #1 -X +1, Y, -Z +1/2
#2 -X +1, -Y +1, -Z +1

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for $TeCl_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Te(1)	13(1)	6(1)	23(1)	1(1)	6(1)	2(1)
Te(2)	13(1)	4(1)	22(1)	1(1)	6(1)	0(1)
Cl(1)	18(1)	8(1)	25(1)	-2(1)	8(1)	0(1)
Cl(2)	17(1)	9(1)	27(1)	0(1)	7(1)	-1(1)
Cl(3)	18(1)	20(1)	23(1)	3(1)	4(1)	2(1)
Cl(4)	19(1)	20(1)	33(1)	3(1)	14(1)	4(1)
Cl(5)	30(1)	6(1)	36(1)	2(1)	13(1)	3(1)
Cl(6)	17(1)	16(1)	24(1)	-1(1)	5(1)	2(1)
Cl(7)	17(1)	13(1)	31(1)	-3(1)	12(1)	-3(1)
Cl(8)	27(1)	5(1)	30(1)	0(1)	13(1)	0(1)

Results and Discussion

Synthesis of $TeCl_4$

In the attempt for preparation adduct Cl_2Te-ICl from the reaction of Te and ICl_3, yellow-green crystals of $TeCl_4$ were obtained. The reaction path way can be as following:

1) $ICl_3 \xrightarrow{\text{heat}} ICl + Cl_2$

2) $Te + 2\,Cl_2 \longrightarrow TeCl_4$

It is clear that at 250 °C, first some ICl_3 dissociate to chlorine and iodine chlroride. Then tellurium reacts with fresh chlorine and forms yellow-green crystalline compound $TeCl_4$, which are separated from the vapour phase in the cold side of the ampoule.

Crystal Structure of $TeCl_4$

The structure consists of isolated tetramers Te_4Cl_{16} which have only Cl .... Cl van der Waals contacts to neighboring Te_4Cl_{16} molecular units. These tetramers have a cubane-like structure with Te and Cl atoms occupying alternatively the corners of Te_4Cl_4

cubane skeleton. Figure 1 shows the unit cell, Figure 2 shows a detailed view of structure and the connection of atoms, and Table 3 shows bond length and bond angles.

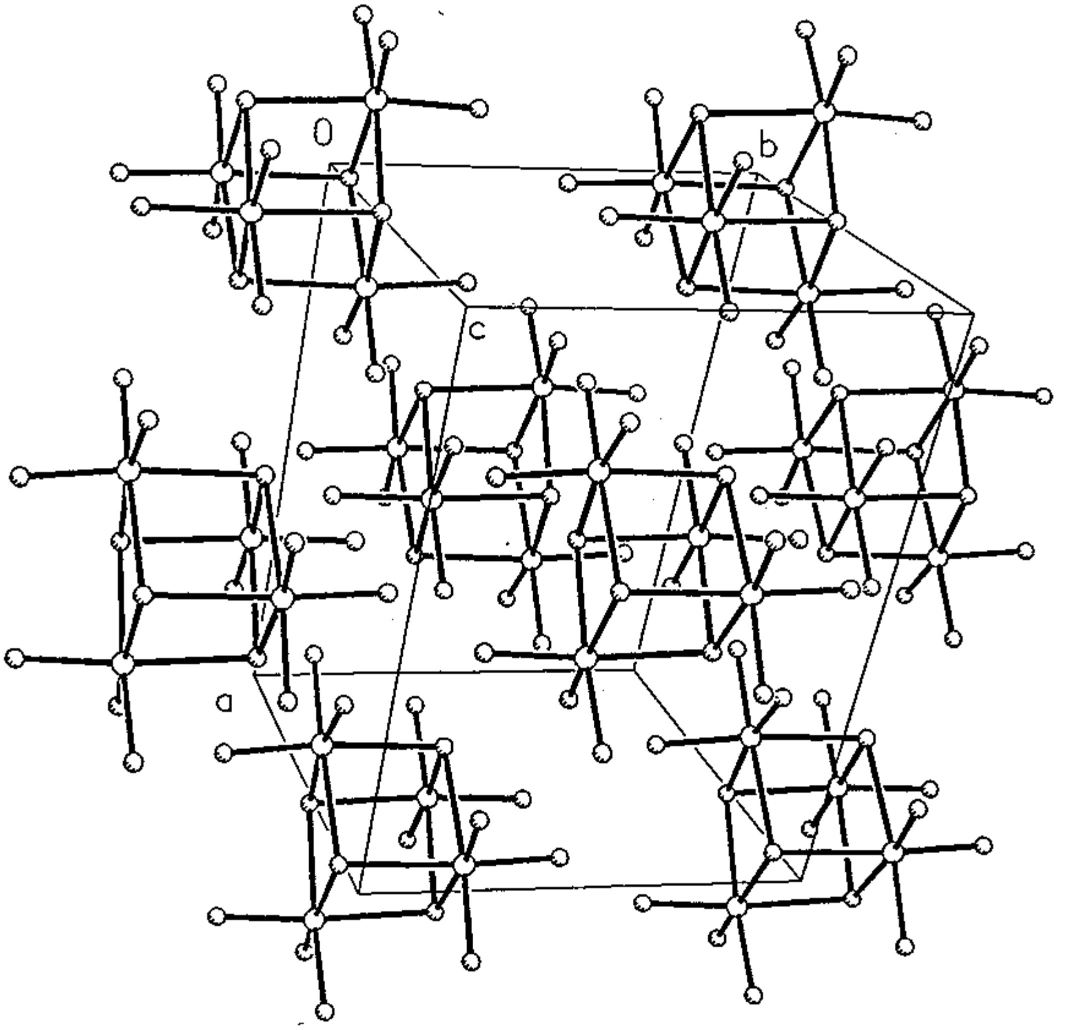

Figure 1 . Representation of the unit cell of Te_4Cl_{16}.

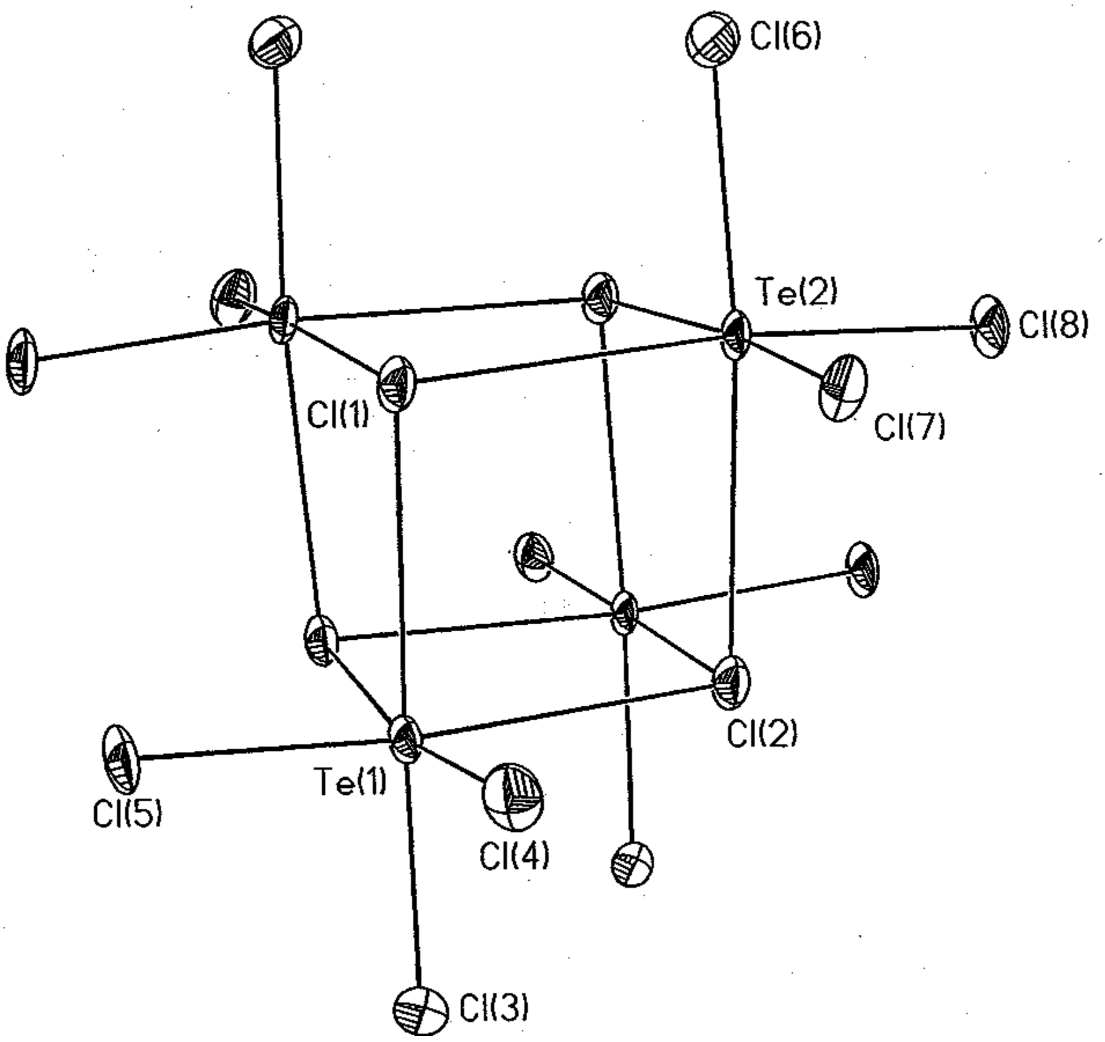

Figure 2. Perspective view of the structure of Te_4Cl_{16} group.

In fact is built of $TeCl_3^+$ and of Cl^- ions with strong cation-anion interaction (average 2.90 Å). Every Te atom has three terminal atoms at an average bond distance of 2.325 Å. Together with these it forms an equilateral trigonal pyramid with mean bond angles Cl-Te-Cl of 95.06 °. Comparable values are found in $TeCl_3MoOCl_4$ [27] (Te-Cl 2.302 Å, Cl-Te-Cl 95.4 °) , $(TeCl_3)_2MoCl_6$ (Te-Cl 2.311 Å, Cl-Te-Cl 95.13°), and $(TeCl_3)_2ReCl_6$ [28] (Te-Cl 2.303 Å, Cl-Te-Cl 95.13°).

Like in nearly all compounds containing TeX_3^+ (X = F, Cl, Br, I) strong cation-anion interaction were observed in [$(TeCl_3^+)$ Cl^-]. The coordination of Te is completed to a strongly distorted octahedron by three bridging Cl atoms of Te_4Cl_4 cube with much longer bond distances (average 2.915 Å) and mean bond angles (Cl-Te-Cl) of 85.50°. Comparable Te-Cl bond length values are found 2.938 Å, 2.929 Å and 2.941 Å in the $TeCl_3MoOCl_4$ [27] , $(TeCl_3)_2MoCl_6$,and $(TeCl_3)_2ReCl_6$ [28] respectively. This distortion of $TeCl_6$ octahedron active lone pair electron on the tellurium atom sticking out forward the longer distant face of the octahedron.

The low-temperature structure of $TeCl_4$ was similar in all essential details with earlier studied [29] at room temperature. However, our low-temperature experiment allowed improving substantially the accuracy of the final geometrical parameters.

Since, $TeCl_4$ have a partially ionic character, which enables it to react with strong Lewis acid to form ionic adducts. The role of the halide ion acceptor can be filled not only by halides of main group elements like $AlCl_3$, $BiCl_3$, AsF_6 or SbF_6, but by metal halides of subgroup element as well, such as $TiCl_4$, $NbCl_5$, $FeCl_3$, UCl_5, $MoOCl_4$, $ReCl_4$, or $AuCl_3$, $MoOCl_3$, $VOCl_3$ also proved to be a suitable Lewis acid. So far compounds $TeCl_3MoOCl_4$ [27] $(TeCl_3)_2MoCl_6$ [28], $TeCl_3MCl_6$ [30] (M = Sb, Nb, Ta) were prepared by acid-base Lewis adducts.

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Povzetek

Navedena je nova metoda sinteze telurjevega tetraklorida iz jodovega triklorida in telurja v evakuirani stekleni ampuli pri 250 °C. Nastanejo za rentgensko strukturno analizo primerni kristali. Ponovno je določena struktura pri 100 K. Strukturo sestavljajo tetrameri Te_4Cl_{16}, ki imajo kubanu podobno zgradbo. Telurjev atom je obdan s tremi klorovimi atomi s poprečno razdaljo 2.325 Å, oktaedrično koordinacijo pa dopoljnjujejo še trije mostovni klorovi atomi na poprečni razdalji 2.915 Å.