differences from 90° in the Cl—Tc—Cl bond angles. It is reasonable to relate these effects to the presence of the $[AsPh_4]^+$ cations in the crystal lattice, and indeed close Cl···H contacts of *ca* 2·8 Å, and Cl···C contacts of *ca* 3·5 Å, occur with each chlorine atom. The sum of van der Waals radii for chlorine and hydrogen is 3·0 Å (Pauling, 1960). It seems likely, therefore, that crystal-packing forces resulting from the presence of the bulky $[AsPh_4]^+$ cations, rather than electronic effects, are the cause of the small tetragonal distortion in the $[TcCl_6]^{2-}$ anion in this compound.

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References

BALDAS, J., BOAS, J. F., BONNYMAN, J. & WILLIAMS, G. A. (1984). *J. Chem. Soc. Dalton Trans.* In the press.

BANDOLI, G., CLEMENTE, D. A., MAZZI, U. & RONCARI, E. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1381–1384.

BANDOLI, G., MAZZI, U., RONCARI, E. & DEUTSCH, E. (1982). *Coord. Chem. Rev.* **44**, 191–227.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

ELDER, M., FERGUSSON, J. E., GAINSFORD, G. J., HICKFORD, J. H. & PENFOLD, B. R. (1967). *J. Chem. Soc. A*, pp. 1423–1425.

ELDER, M. & PENFOLD, B. R. (1966). *Inorg. Chem.* **5**, 1197–1200.

ELDER, R. C., ESTES, G. W. & DEUTSCH, E. (1979). *Acta Cryst.* B**35**, 136–137.

GRANT, D. F., GABE, E. J. & LE PAGE, Y. (1978). *GLSOR. Least-Squares Orientation Matrix Program.* National Research Council of Canada, Ottawa.

HOPPE, W. (1965). *Angew. Chem. Int. Ed. Engl.* **4**, 508–516.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 100. Birmingham: Kynoch Press.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

KOZ'MIN, P. A. & NOVITSKAYA, G. N. (1975). *Koord. Khim.* **1**, 473–476.

KOZ'MIN, P. A., NOVITSKAYA, G. N. & KUZINA, A. F. (1972). *Zh. Strukt. Khim.* **13**, 941–942.

MAZZI, U., RONCARI, E., BANDOLI, G. & CLEMENTE, D. A. (1982). *Transition Met. Chem.* **7**, 163–166.

PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 260. Ithaca: Cornell Univ. Press.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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Structure of Tris(cyclohexylammonium) Chloride Tetrachlorocobaltate(II), $(C_6H_{14}N)_3Cl(CoCl_4)$

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Abstract. $M_r = 536·75$, monoclinic, $P2_1/c$, $a = 15·365\,(6)$, $b = 10·180\,(5)$, $c = 22·042\,(9)$ Å, $\beta = 127·84\,(2)°$, $V = 2722·8$ Å^3, $Z = 4$, $D_x = 1·309$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 1·15$ mm^{-1}, $F(000) = 1147$, $T = 293\,(2)$ K, wR (R) = 0·056 (0·070) for 1376 observed reflections. The structure consists of slightly distorted $CoCl_4^{2-}$ tetrahedra, connected by hydrogen bonds through cyclohexylammonium groups into chains along **c**, and *via* two amine nitrogen atoms and an uncoordinated chloride along **b**. All cyclohexyl rings are in the chair conformation.

Introduction. In recent years we have been successful in synthesizing materials with ferromagnetic interactions predominantly in one direction (Willett, Gaura & Landee, 1983; Willett & Landee, 1981). In particular, the compound cyclohexylammonium trichlorocuprate(II), for short CHAC (Groenendijk, Blöte, Van Duyneveldt, Gaura, Landee & Willett, 1981), attracted quite some interest in the solid-state physics community (Kopinga, Tinus & de Jonge, 1982; Poertadji, Ablart, Pescia, Clément & Cheik-Rouhou, 1983). We therefore tried to synthesize the corresponding cobalt(II) salt. In the course of these investigations we obtained the compound tris(cyclohexylammonium) chloride tetrachlorocobaltate(II), CHCO, which promises to have interesting magnetic properties, even though its structure is not related to CHAC.

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Experimental. Crystals grown from 1:1 ethanol–water solution containing cobalt(II) chloride and cyclohexylammonium chloride in 1:1 molar ratio, and a small amount of hydrochloric acid, by slow evaporation. Triangular-prismatic crystal (0·14 mm edges, 0·36 mm long) used for data collection, Picker automated diffractometer. Angular settings of 12 carefully centered reflections ($2\theta \simeq 30°$) used to optimize lattice parameters and crystal orientation. Absorption correction applied, transmission factors showing very little variation (0·90–0·92) owing to small absorption coefficient. Data collected for all h, $k \le 0$, $l \ge 0$, $(\sin\theta)/\lambda \le 0{\cdot}807$ Å^{-1}. Three standards ($\bar{1}$,0,10, 60$\bar{2}$, 0$\bar{4}$0) monitored after every 41 reflections, variation within counting statistics. 1950 reflections collected, 1732 unique and allowed by symmetry, 1376 with $F(\mathrm{obs}) > 2\sigma[F(\mathrm{obs})]$. Cobalt and chlorine atom positions obtained by direct methods. Carbon, nitrogen and, at a later stage, hydrogen found on subsequent difference maps. Full-matrix least-squares refinement, based on F, $w = 1/\sigma^2$, one scale factor, positional and anisotropic thermal parameters for non-hydrogen atoms and positional parameters for hydrogens on the last cycles, 370 variables. Hydrogen positions agreed with calculated values for all H(C). $R = 0{\cdot}070$, $wR = 0{\cdot}056$, $S = 1{\cdot}22$. Final difference Fourier synthesis featureless, extrema 0·44 and −0·38 e Å^{-3}. Av. $\Delta/\sigma = 0{\cdot}071$, max. $\Delta/\sigma = 0{\cdot}26$ for non-hydrogen parameters.* Scattering factors from *International Tables for X-ray Crystallography* (1962) for Co^{2+}, Cl^-, N, C, and from Stewart, Davidson & Simpson (1965) for H. Computer program library included locally adapted versions of: *ORABS* (Wehe, Busing & Levy, 1962), *ORFLS* (Busing, Martin & Levy, 1962), *MULTAN* (Main, Germain & Woolfson, 1972), *ORFFE* (Busing, Martin & Levy, 1964), *ALFF* (Hubbard, Quicksall & Jacobson, 1971) and *ORTEP* (Johnson, 1965).†

Table 1. *Fractional coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^3) *of the non-hydrogen atoms*

$U_{eq} = (U_1 + U_2 + U_3)/3$, U_i being an eigenvalue of the **U** matrix.

	x	y	z	U_{eq}
Co	1050 (1)	2472 (2)	6094·8 (9)	51 (1)
Cl(1)	1445 (3)	317 (3)	6172 (2)	63 (2)
Cl(2)	1867 (3)	3629 (3)	7190 (2)	66 (2)
Cl(3)	1333 (3)	3469 (4)	5316 (2)	83 (2)
Cl(4)	−819 (2)	2629 (3)	5452 (2)	60 (1)
Cl(5)	9659 (2)	2332 (3)	7994 (2)	49 (1)
N(1)	1073 (10)	734 (12)	4455 (7)	54 (5)
N(2)	9333 (10)	576 (11)	1760 (7)	48 (5)
N(3)	8368 (10)	3583 (12)	3685 (6)	54 (5)
C(11)	2129 (12)	563 (12)	4563 (9)	42 (6)
C(12)	1917 (11)	−223 (14)	3913 (7)	47 (6)
C(13)	3024 (15)	−539 (16)	4058 (10)	75 (8)
C(14)	3835 (14)	−1162 (18)	4826 (13)	87 (9)
C(15)	4039 (12)	−244 (19)	5447 (8)	71 (8)
C(16)	2973 (12)	−14 (16)	5338 (9)	63 (7)
C(21)	8150 (12)	379 (13)	1392 (8)	45 (6)
C(22)	8028 (12)	−327 (16)	1937 (8)	62 (6)
C(23)	6837 (16)	−575 (17)	1575 (11)	79 (9)
C(24)	6304 (13)	−1388 (19)	859 (15)	96 (10)
C(25)	6407 (14)	−756 (20)	291 (10)	93 (10)
C(26)	7620 (14)	−402 (16)	656 (9)	62 (8)
C(31)	7262 (13)	3053 (14)	3341 (9)	58 (7)
C(32)	6680 (14)	2816 (17)	2500 (9)	78 (8)
C(33)	5526 (20)	2276 (20)	2114 (12)	121 (12)
C(34)	4884 (18)	2971 (24)	2320 (13)	122 (13)
C(35)	5510 (18)	3228 (19)	3144 (14)	99 (10)
C(36)	6602 (15)	3838 (18)	3507 (8)	71 (9)

Discussion. Final atomic positional and equivalent isotropic thermal parameters are listed in Table 1. Fig. 1 shows the atomic labeling and non-hydrogen interatomic distances and angles for the $CoCl_4^{2-}$ anion and the three individual cyclohexylammonium ions. A compilation of geometrical parameters of the former in seven crystal structures was given by Antolini, Marcotrigiano, Menabue & Pellacani (1979). In addition at least ten more structure determinations of salts containing $CoCl_4^{2-}$ have been published (Bombieri, Forsellini, Del Pra & Tobe, 1980; Clay, Murray-Rust & Murray-Rust, 1976; Fronczek, Majestic, Newkome, Hunter & Atwood, 1981; Hinamoto, Ooi & Kuroya, 1971; van Loon & Visser, 1977; MacDonald & Trotter, 1974; Prout & Murray-Rust, 1969; Søtofte & Nielsen, 1981; Trotter & Whitlow, 1970; Vance, Holt, Pierpont & Holt, 1980; Vermin, Verschoor & IJdo, 1976). In all these salts, as in the present structure, the anion has a distorted tetrahedral coordination geometry. The nature of these distortions, however, does not follow a recognizable trend. In addition, most theories predict exact tetrahedral coordination for the isolated complex. Thus, we believe that the distortions are not intrinsic, but rather due to hydrogen bonding and electrostatic effects in the crystal. δ' and δ angles in the sense of Muetterties & Guggenberger (1974) are: δ'_{12} [dihedral angle along the tetrahedron edge between Cl(1) and Cl(2)] = 109·3 (1), δ'_{34} [between Cl(3) and Cl(4)] = 105·3 (1); $\delta_{13} = 110{\cdot}9$ (1), $\delta_{14} = 110{\cdot}1$ (1), $\delta_{23} = 110{\cdot}5$ (1), $\delta_{24} = 110{\cdot}6$ (1)°. These angles would be 109·5° in a regular tetrahedron, or 0 (δ') and 180° (δ) for a square-planar complex. The complex with the cyclohexylammonium salt is best described as C_{2v}-distorted, with the pseudo twofold axis crossing the Cl(1)–Cl(2) and the Cl(3)–Cl(4) vectors. The Cl(1)—Co—Cl(2) angle is opened up with respect to the tetrahedral angle, whereas the Cl(3)—Co—Cl(4) angle is reduced. At the same time the Co—Cl(1) and Co—Cl(2) distances are smaller than the Co—Cl(3) and Co—Cl(4)

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* Except N(3) parameters, where Δ/σ averages 0·37, indicating the possibility of disorder.

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39401 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

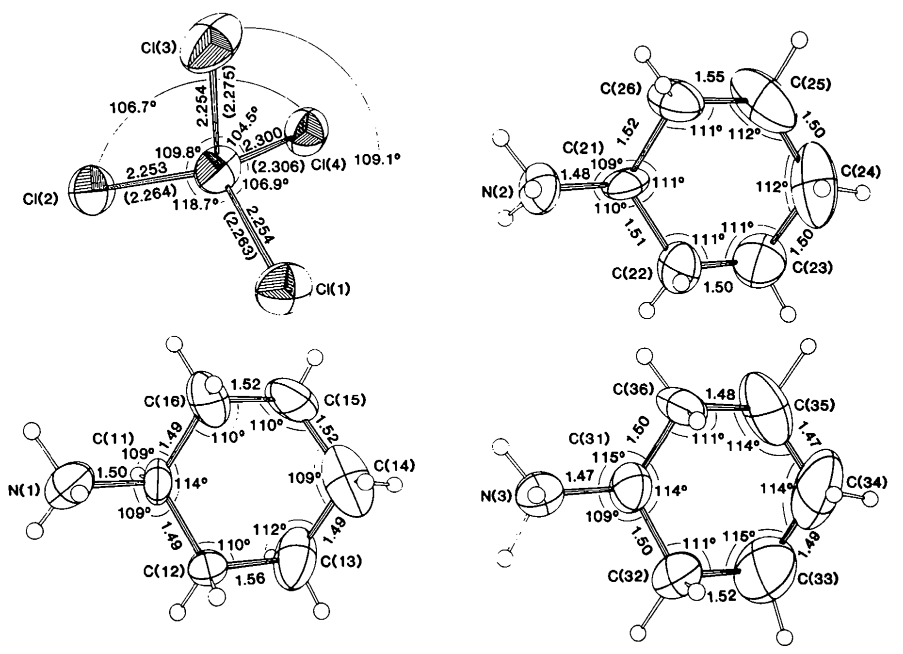

Fig. 1. Atom labels, interatomic distances (Å) and angles (°) of the $CoCl_4^{2-}$ and the $C_6H_{11}NH_3^+$ ions. Distances in parentheses are corrected for thermal motion (chlorines riding on cobalt). E.s.d. for $CoCl_4^{2-}$: 0·004 Å and 0·1°; for cyclohexylammonium: 0·02 Å and 1°. The ellipsoids are drawn at the 50% probability limit.

distances, using the thermally corrected (Busing & Levy, 1964) values. The deviations from tetrahedral, as well as the distances, are well within the range spanned by the above mentioned salts containing $CoCl_4^{2-}$. The closest match is probably with the benzotriazolium salt (Søtofte & Nielsen, 1981), even though there the distortion is larger.

The closest contacts between $CoCl_4^{2-}$ tetrahedra are along the y axis. Nearest neighbors are related by two inequivalent inversion operations, leaving the possibility of an alternating-chain magnet. The two inequivalent interactions are through hydrogen bonding across R—NH_3 groups (Fig. 2). In bridge A the ammonium group N(1) connects Cl(4) and Cl(1) of one anion with Cl(3) and Cl(1) of another. Both hydrogen bonds appear bifurcated, even though the errors in the H parameters do not allow an in-depth analysis (Table 2). The third hydrogen atom on N(1) is directed toward an ionic chloride Cl(5). Bridge B is through N(3), connecting Cl(4) with Cl(2) of an adjacent $CoCl_4^{2-}$. Again, the third hydrogen is directed to a Cl(5) ion. The hydrogen atoms of N(2) are pointing towards Cl(4) and two different Cl(5) atoms.

The main interaction between the chains is along the z direction. The lattice chloride Cl(5) connects N(2) associated with one chain with N(1), N(2), and N(3) of another chain. As seen in Fig. 3, the only interactions along the x direction are van der Waals contacts between cyclohexyl residues. Magnetic interactions in that direction are expected to be purely dipolar.

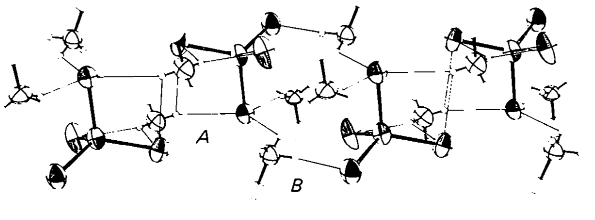

Fig. 2. The chain-like arrangement of nearest-neighbor $CoCl_4^{2-}$ tetrahedra with hydrogen-bonded cyclohexylammonium groups. Only the first carbon atoms of the latter are drawn (open ellipses). The letters A and B refer to the two inequivalent bridges as described in the text.

Table 2. *Hydrogen bonding between* $CoCl_4^{2-}$, Cl^- *and* $C_6H_{11}NH_3^+$ *units*

Bifurcated hydrogen bonds are indicated by a brace.

	d(Cl–N), Å	d(Cl–H), Å
Cl(1)···H(1^{i})–N(1^{i})	3·39 (1)	2·9 (1)
Cl(4)···H(1^{i})–N(1^{i})	3·47 (1)	2·7 (1)
Cl(1)···H(3)–N(1)	3·49 (1)	2·8 (1)
Cl(3)···H(3)–N(1)	3·25 (1)	3·0 (1)
Cl(2)···H(3^{ii})–N(3^{ii})	3·32 (1)	2·4 (1)
Cl(4)···H(2^{vi})–N(2^{vi})	3·30 (1)	2·4 (1)
Cl(4)···H(1^{iii})–N(3^{iii})	3·42 (1)	2·9 (1)
Cl(5)···H(2)–N(3)	3·29 (1)	2·2 (1)
Cl(5)···H(3)–N(2)	3·24 (1)	2·4 (1)
Cl(5)···H(1^{iv})–N(2^{iv})	3·23 (1)	2·4 (1)
Cl(5)···H(2^{v})–N(1^{v})	3·22 (1)	2·5 (1)

Symmetry code: (i) $-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x-1, y, z$; (iv) $2-x, -y, 1-z$; (v) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $x-1, \frac{1}{2}-y, \frac{1}{2}+z$.

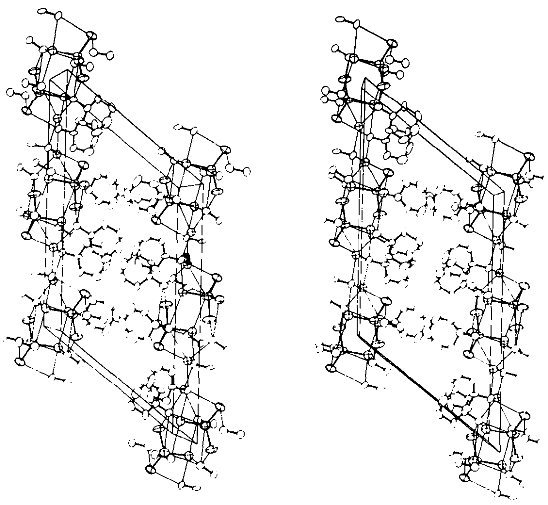

Fig. 3. Stereoview approximately along the b axis. The c axis is vertical. Hydrogen-bonded Cl–N contacts are indicated by single lines. Co and Cl are drawn with principal ellipses. Cyclohexyl rings outside the unit cell and hydrogens are omitted for clarity.

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References

Antolini, L., Marcotrigiano, G., Menabue, L. & Pellacani, G. C. (1979). *Inorg. Chem.* **18**, 2652–2658.

Bombieri, G., Forsellini, E., Del Pra, A. & Tobe, M. L. (1980). *Inorg. Chim. Acta*, **40**, 71–77.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142–146.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

Clay, R. M., Murray-Rust, J. & Murray-Rust, P. (1976). *Acta Cryst.* B**32**, 111–114.

Fronczek, F. R., Majestic, V. K., Newkome, G. R., Hunter, W. E. & Atwood, J. L. (1981). *J. Chem. Soc. Perkin Trans.* 2, pp. 331–335.

Groenendijk, H. A., Blöte, H. W. J., Van Duyneveldt, A. J., Gaura, R. M., Landee, C. P. & Willett, R. D. (1981). *Physica* (*Utrecht*), **106** B, 47–58.

Hinamoto, M., Ooi, S. & Kuroya, H. (1971). *Bull. Chem. Soc. Jpn*, **44**, 586.

Hubbard, C. R., Quicksall, C. O. & Jacobson, R. A. (1971). *ALFF*. Report IS-2625. Iowa State Univ. and Institute for Atomic Research, Ames, Iowa.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kopinga, K., Tinus, A. M. C. & de Jonge, W. J. M. (1982). *Phys. Rev. B*, **25**, 4685–4690.

Loon, C. J. J. van & Visser, D. (1977). *Acta Cryst.* B**33**, 188–190.

MacDonald, A. L. & Trotter, J. (1974). *Can. J. Chem.* **52**, 734–737.

Main, P., Germain, G. & Woolfson, M. M. (1972). *MULTAN72. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Muetterties, E. L. & Guggenberger, L. J. (1974). *J. Am. Chem. Soc.* **96**, 1748–1756.

Poertadji, S., Ablart, G., Pescia, J., Clément, S. & Cheik-Rouhou, A. (1983). *J. Phys.* (*Paris*), **44**, L561–L566.

Prout, C. K. & Murray-Rust, P. (1969). *J. Chem. Soc. A*, pp. 1520–1525.

Søtofte, I. & Nielsen, K. (1981). *Acta Chem. Scand. Ser. A*, **35**, 739–745.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Trotter, J. & Whitlow, S. H. (1970). *J. Chem. Soc. A*, pp. 460–464.

Vance, T. B. Jr, Holt, E. M., Pierpont, C. G. & Holt, S. L. (1980). *Acta Cryst.* B**36**, 150–153.

Vermin, W. J., Verschoor, G. C. & IJdo, D. J. W. (1976). *Acta Cryst.* B**32**, 3325–3328.

Wehe, D. J., Busing, W. R. & Levy, H. A. (1962). *ORABS*. Report ORNL-TM-229. Oak Ridge National Laboratory, Tennessee.

Willett, R. D., Gaura, R. M. & Landee, C. P. (1983). *Extended Linear Chain Compounds*, Vol. 3, edited by J. S. Miller, pp. 143–191. New York: Plenum.

Willett, R. D. & Landee, C. P. (1981). *J. Appl. Phys.* **52**, 2004–2009.

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Structure of Dichlorobis(*p*-methoxyphenyl)tellurium(IV), $[TeCl_2(C_7H_7O)_2]$

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Abstract. $M_r = 412\cdot6$, triclinic, $P\bar{1}$, $a = 10\cdot243\ (5)$, $b = 12\cdot480\ (4)$, $c = 13\cdot654\ (4)$ Å, $\alpha = 109\cdot22\ (2)$, $\beta = 80\cdot42\ (3)$, $\gamma = 77\cdot30\ (3)^\circ$, $V = 1553\ (1)$ Å^3, $Z = 4$, $D_x = 1\cdot76$, $D_m = 1\cdot74$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 2\cdot09$ mm^{-1}, $F(000) = 800$, $T = 294$ K, final $R = 0\cdot028$ for 3406 unique observed reflections. The structure consists of isolated step-like tetramers in which two independent molecules and their centrosymmetric equivalents are linked through Te···Cl secondary interactions. The Te–C and Te–Cl bonds occupy

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