$K_4Ti_3Te_9$ – A New Pseudo One-Dimensional Polyanionic Alkali Chalcogenometallate(IV)

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Lustrous black needle shaped single crystals of $K_4Ti_3Te_9$ were obtained by reacting K_2Te with the corresponding elemental components at 1000 °C. $K_4Ti_3Te_9$ is monoclinic, $mP64$, s. g. $P2_1/c$ (No. 14), $Z = 4$ with $a = 9.052(2)$, $b = 8.088(1)$, $c = 29.465(9)$ Å, $\beta = 92.35(1)^\circ$. The crystal structure was determined from diffractometer data and refined to a conventional R value of 0.035 (2840 F_o's, 146 variables). The compound contains undulating polyanionic chains built up by severely distorted $TiTe_6$ octahedra sharing opposite faces which run parallel to [100] and are arranged in a hexagonal rod packing. The translation period comprises three octahedra. The most striking feature of this compound is the formation of two ditelluride groups per formula unit with unusually long Te-Te distances of 2.960(2) and 3.025(2) Å, respectively. All other Te-Te distances start at 3.2 Å. The nearest homonuclear neighbours of the two pairs are at 3.215(2) and 3.333(2) Å apart. Ti-Te bond lengths range from 2.700(3) to 2.841(3) Å with an average value of 2.772(4) Å for all three crystallographically independent titanium atoms. The alkali cations are irregularly coordinated by 7 to 9 tellurium atoms.

Key words: Chalcogenides, Polyanionic Chains, Group IVa Metal Compounds

Introduction

A large number of polychalcogenides $A_mT_n^{IV}Q_o$ (A = Na – Cs, Tl; T = Ti, Zr, Hf; Q = S, Se, Te) with pseudo one-dimensional structures has been reported during the last decade. They comprise the sulfides, Tl_2TiS_4 [1], K_2ZrS_4, Rb_2ZrS_4, Rb_2HfS_4 [2], $K_2Ti_2S_9$ [3], $Cs_2Ti_2S_9$ [4], $A_4Ti_3S_{14}$, (A = K – Cs) [5, 6], $Cs_4Zr_3S_{14}$ [7], $Rb_4Hf_3S_{14}$ [6], the selenides $Na_2Ti_2Se_8$ [8], $Cs_4Ti_3Se_{13}$ [6], $Na_2Ti_2Se_9$ [9], $Rb_4Ti_3Se_{13}$ [10], $K_4Hf_3Se_{14}$ [7], $Rb_4Zr_3Se_{14}$, $Rb_4Hf_3Se_{14}$ [10], $Cs_4Zr_3Se_{14}$ [6], $Cs_4Hf_3Se_{14}$ [6], $K_4Zr_3Se_{15}$ [11] and finally the tellurides $Rb_3Ti_3Te_{11}$ [12], $Cs_3Ti_3Te_{11}$ [13], $Cs_4Hf_3Te_{13}$ [14], $Cs_5Hf_5Te_{26}$ [15], $Cs_4Zr_3Te_{16}$ [16], $Rb_4Zr_3Te_{16}$ [17], $Rb_4Hf_3Te_{16}$ [10], $K_4Zr_3Te_{17}$ [14] and $K_4Hf_3Te_{17}$ [18]. Out of these the tellurides merit particular interest since they show the widest range of polyanionic compositions and are invariably characterized by partial Te-Te bonds. It was therefore of interest to find out whether this peculiarity persists at even lower tellurium contents. This led to the preparation of $K_4Ti_3Te_9$ – which coming close to the normal valence composition K_2TiTe_3 represents the lowest member of this polyanionic series so far.

Table 1. Crystallographic data for $K_4Ti_3Te_9$.

Pearson Symbol	$mP64$
a[Å]	9.052(2)
b[Å]	8.008(1)
c[Å]	29.465(9)
β [°]	92.35(1)
Space group	$P2_1/c$ (No. 14)
Z	4
V [Å^3]	2134.1
d_x [gcm^{-3}]	4.51
M_r	1448.51
μ(Mo-K$_\alpha$) [cm^{-1}]	139.50
Structure refinement:	
Unique reflections	4620
Observed reflections	2840
Cutoff	$3.00\sigma(F_o)^2$
Variables	146
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	0.037
$R_w = \left[\sum w \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2 / \sum w \lvert F_o\rvert^2\right]^{1/2}$	0.035
$w = \left[\sigma(F_o^2)^2 + (0.05F_o^2)^2\right]^{-1/2}$	
Residual electron density [eÅ^{-3}]	1.69/–0.67

Table 2. Positional parameters and thermal displacement factors for $K_4Ti_3Te_9$. (All atoms lie on the Wyckoff position 4*e*.)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}*
K(1)	0.3881(5)	0.2360(5)	0.4837(1)	0.036(2)	0.040(3)	0.028(2)	−0.003(2)	0.009(2)	−0.000(2)	2.73(8)
K(2)	0.9327(5)	0.2093(7)	0.4347(2)	0.035(2)	0.054(3)	0.041(2)	0.002(2)	−0.002(2)	−0.007(2)	3.43(9)
K(3)	0.1308(5)	0.2352(7)	0.7671(2)	0.039(2)	0.066(3)	0.030(2)	−0.014(2)	0.006(2)	0.006(2)	3.6(1)
K(4)	0.5719(5)	0.2174(7)	0.3170(2)	0.040(2)	0.059(3)	0.039(2)	−0.003(2)	−0.010(2)	0.010(2)	3.60(9)
Ti(1)	0.9201(3)	0.1853(4)	0.1306(1)	0.011(1)	0.030(1)	0.026(1)	0.001(1)	0.0020(9)	0.002(1)	1.74(5)
Ti(2)	0.2515(4)	0.2641(4)	0.6271(1)	0.010(1)	0.034(2)	0.024(1)	−0.001(1)	−0.001(1)	0.002(1)	1.71(5)
Ti(3)	0.5831(3)	0.1948(4)	0.1164(1)	0.009(1)	0.036(2)	0.023(1)	0.000(1)	0.000(1)	−0.000(1)	1.80(5)
Te(1)	0.0670(1)	0.1668(2)	0.05012(4)	0.0178(4)	0.0261(6)	0.0292(5)	0.0012(5)	0.0047(4)	−0.0026(5)	2.30(2)
Te(2)	0.4512(1)	0.1676(2)	0.20012(3)	0.0137(4)	0.0294(6)	0.0257(5)	−0.0017(5)	−0.0009(4)	0.0066(5)	2.16(2)
Te(3)	0.7386(1)	0.1596(2)	0.69238(4)	0.0142(4)	0.0275(6)	0.0262(5)	0.0018(5)	−0.0002(4)	−0.0040(5)	2.30(2)
Te(4)	0.7709(1)	0.1588(2)	0.55504(4)	0.0160(4)	0.0255(6)	0.0298(5)	−0.0000(5)	0.0033(4)	0.0030(5)	2.15(2)
Te(5)	0.4227(1)	0.0258(1)	0.58892(4)	0.0188(4)	0.0460(8)	0.0186(5)	0.0016(6)	0.0024(4)	0.0011(6)	1.88(2)
Te(6)	0.0699(1)	0.0272(1)	0.66196(4)	0.0292(5)	0.0417(7)	0.0182(5)	−0.0084(6)	0.0020(4)	−0.0015(6)	1.88(2)
Te(7)	0.6202(1)	0.0108(1)	0.92600(4)	0.0166(4)	0.0394(7)	0.0267(5)	−0.0021(5)	−0.0006(4)	−0.0106(6)	1.79(2)
Te(8)	0.2533(1)	0.0946(1)	0.87759(4)	0.0207(5)	0.0420(7)	0.0251(5)	0.0004(6)	−0.0014(4)	0.0115(6)	1.87(2)
Te(9)	0.1173(1)	0.9847(1)	0.17529(4)	0.0135(4)	0.0286(5)	0.0302(5)	−0.0008(6)	−0.0021(3)	0.0000(6)	1.81(2)

$$^*B_{eq} = \frac{8\pi^2}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a_i}\mathbf{a_j}.$$

Table 3. Selected interatomic distances and bond angles for $K_4Ti_3Te_9$.

a) Coordination of the alkali cations			
K(1)-Te(3)	3.411(5)	K(2)-Te(4)	3.419(6)
K(1)-Te(3)	3.447(5)	K(2)-Te(3)	3.603(5)
K(1)-Te(1)	3.486(5)	K(2)-Te(6)	3.680(6)
K(1)-Te(1)	3.523(5)	K(2)-Te(6)	3.682(6)
K(1)-Te(9)	3.566(6)	K(2)-Te(9)	3.751(5)
K(1)-Te(8)	3.635(5)	K(2)-Te(1)	3.766(5)
K(1)-Te(6)	3.646(5)	K(2)-Te(8)	3.897(6)
		K(2)-Te(2)	3.924(6)
		K(2)-Te(8)	3.985(6)
K(3)-Te(2)	3.359(5)	K(4)-Te(1)	3.371(6)
K(3)-Te(2)	3.503(6)	K(4)-Te(2)	3.535(6)
K(3)-Te(4)	3.532(6)	K(4)-Te(5)	3.586(6)
K(3)-Te(9)	3.571(6)	K(4)-Te(5)	3.646(6)
K(3)-Te(5)	3.654(5)	K(4)-Te(9)	3.760(6)
K(3)-Te(4)	3.656(6)	K(4)-Te(4)	3.805(5)
K(3)-Te(7)	3.769(6)	K(4)-Te(3)	3.883(6)
b) Geometry of the $^1_\infty[Ti_3Te_9]^{4-}$*-chain*			
Ti(1)-Te(1)	2.723(4)	Ti(1)-Te(4)	2.737(4)
Ti(1)-Te(2)	2.768(4)	Ti(1)-Te(3)	2.788(4)
Ti(1)-Te(6)	2.797(5)	Ti(1)-Te(5)	2.811(5)
Ti(1)-Ti(2)	3.022(5)	Ti(1)-Ti(3)	3.046(5)
Te(3)-Ti(1)-Te(6)	70.3(1)	Te(2)-Ti(1)-Te(5)	75.2(1)
Te(2)-Ti(1)-Te(3)	88.6(1)	Te(1)-Ti(1)-Te(3)	90.6(2)
Te(2)-Ti(1)-Te(6)	90.9(1)	Te(3)-Ti(1)-Te(5)	91.2(1)
Te(2)-Ti(1)-Te(4)	91.5(2)	Te(1)-Ti(1)-Te(4)	91.6(1)
Te(1)-Ti(1)-Te(5)	95.2(1)	Te(4)-Ti(1)-Te(6)	95.5(1)
Te(1)-Ti(1)-Te(6)	98.0(2)	Te(4)-Ti(1)-Te(5)	102.6(2)
Te(5)-Ti(1)-Te(6)	157.3(1)	Te(3)-Ti(1)-Te(4)	165.8(2)
Te(1)-Ti(1)-Te(2)	170.3(2)		
Ti(2)-Te(2)	2.700(3)	Ti(2)-Te(9)	2.740(4)
Ti(2)-Te(6)	2.763(3)	Ti(2)-Te(7)	2.788(3)
Ti(2)-Te(4)	2.801(4)	Ti(2)-Te(8)	2.834(3)
Ti(1)-Ti(3)	3.046(5)	Ti(2)-Ti(3)	3.059(3)
Te(6)-Ti(2)-Te(8)	65.4(1)	Te(4)-Ti(2)-Te(7)	73.2(1)
Te(2)-Ti(2)-Te(9)	85.3(1)	Te(2)-Ti(2)-Te(4)	91.6(1)
Te(8)-Ti(2)-Te(9)	92.2(1)	Te(7)-Ti(2)-Te(8)	92.4(1)
Te(2)-Ti(2)-Te(6)	93.1(1)	Te(7)-Ti(2)-Te(9)	94.0(1)
Te(4)-Ti(2)-Te(6)	94.8(1)	Te(4)-Ti(2)-Te(8)	96.1(1)
Te(6)-Ti(2)-Te(9)	100.1(1)	Te(2)-Ti(2)-Te(7)	109.9(1)
Te(6)-Ti(2)-Te(7)	154.0(2)	Te(2)-Ti(2)-Te(8)	157.7(1)
Te(4)-Ti(2)-Te(9)	164.9(1)		
Ti(3)-Te(3)	2.725(4)	Ti(3)-Te(9)	2.747(4)
Ti(3)-Te(1)	2.763(4)	Ti(3)-Te(8)	2.780(3)
Ti(3)-Te(5)	2.791(3)	Ti(3)-Te(7)	2.841(3)
Te(5)-Ti(3)-Te(7)	63.4(1)	Te(1)-Ti(3)-Te(8)	78.4(1)
Te(3)-Ti(3)-Te(9)	82.7(1)	Te(1)-Ti(3)-Te(3)	91.1(1)
Te(7)-Ti(3)-Te(8)	92.4(1)	Te(7)-Ti(3)-Te(9)	92.6(1)
Te(3)-Ti(3)-Te(5)	92.9(1)	Te(8)-Ti(3)-Te(9)	93.2(1)
Te(1)-Ti(3)-Te(5)	94.7(1)	Te(5)-Ti(3)-Te(9)	97.1(1)
Te(1)-Ti(3)-Te(7)	97.7(1)	Te(3)-Ti(3)-Te(8)	112.1(1)
Te(5)-Ti(3)-Te(8)	154.0(2)	Te(3)-Ti(3)-Te(7)	155.2(1)
Te(1)-Ti(3)-Te(9)	166.9(1)		
c) Te-Te distances up to 3.8 Å			
Te(5)-Te(7)	2.960(2)	Te(6)-Te(8)	3.025(2)
Te(3)-Te(6)	3.215(2)	Te(4)-Te(7)	3.333(2)
Te(2)-Te(5)	3.403(2)	Te(1)-Te(8)	3.503(2)
Te(3)-Te(9)	3.616(1)	Te(2)-Te(9)	3.687(1)

Experimental Section

The title compound was prepared from high purity elements (K: 99.9%, Ti: 99.6% and Te 99.999%; Strem Chemicals). As a first step of the synthesis, K_2Te was obtained by reacting the constituent elements in liquid ammonia. Stoichiometric amounts of the powdered educts were intimately mixed in an argon glove box and sealed into a silica ampoule under a vacuum of 10^{-2} Pa. Thermal treatment consisted of gradually heating to 1000 °C, annealing for 1 d

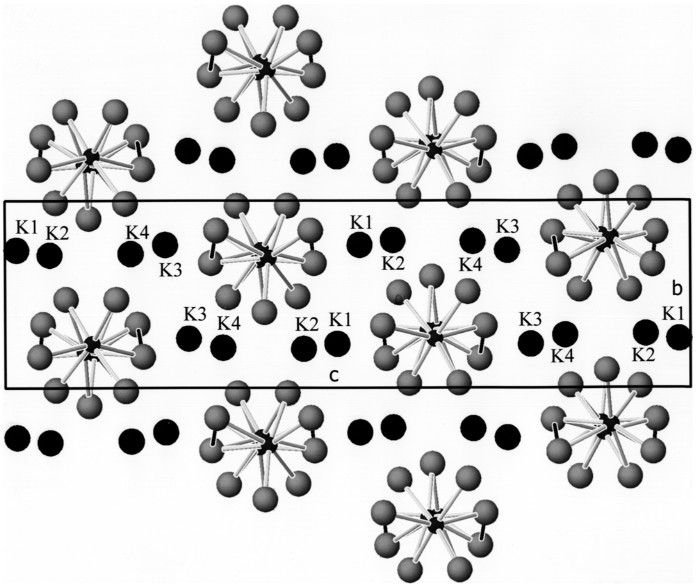

Fig. 1. Projection of the crystal structure of $K_4Ti_3Te_9$ showing the hexagonal rod packing of the anionic chains. The K atoms are represented by full, Ti and Te atoms by small or large shaded circles, respectively.

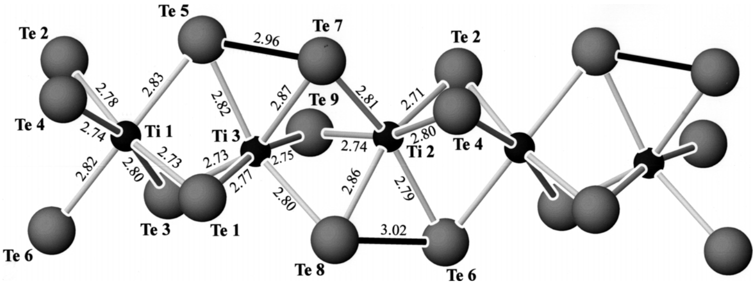

Fig. 2. Bond lengths in the $[Ti_3Te_9]^{4-}$ chain up to 3.2 Å. Homonuclear bonds are represented by full rods.

followed by controlled cooling to ambient temperature at a rate of -2 °C h^{-1}. The reaction product consisted of lustrous needle shaped crystals which were very sensitive to air and humidity and had hence to be handled under inert conditions.

For the structure determination a specimen with the dimensions $0.2 \times 0.06 \times 0.025$ mm^3 was selected, embedded in a thin walled glass capillary and transferred to a kappa diffractometer (*Nonius Turbo CAD4*) operated with graphite monochromated Mo-K$_\alpha$-radiation ($\lambda = 0.71073$ Å).

Results of preliminary crystallographic investigations indicated monoclinic symmetry; systematic extinctions: $0k0$: $k \neq 2n$, $h0\ell$: $\ell \neq 2n$ unambiguously led to space group $P2_1/c$.

The collection of the intensity data was performed at room temperature (21(1) °C) over one quadrant of the reflection sphere ($0 < 2\vartheta < 54°$, $\omega - 2\vartheta$ scans, maximum scan time 80 s, scan width 1.20° + 0.35° tanϑ). Crystal and orientational stability were monitored through the periodic determination of three control reflections which, however, showed only statistical fluctuations of their intensities. The intensity data were corrected for Lorentz- and polarization effects. Merging symmetry equivalent reflections ($R_{int} = 0.042$) led to a unique set of 4620 observations out of which 2840 with $I > 3\sigma(I)$ were considered as significant.

The crystal structure was solved by direct methods (Multan 88 [19]) yielding the positions of the heavier atoms. The potassium atoms were located from subsequent difference Fourier syntheses. Anisotropic refinement of the complete structure converged rapidly to a final residual of 0.037. A final difference Fourier map was featureless. All calculations were performed with programs of the MolEN-crystallographic software package [20]. Absorptions effects were taken into account by empirical correction [21].

Precise lattice constants were obtained by refining the setting angles of 25 reflections with $28° \leq 2\vartheta \leq 36°$. They are given in Table 1 together with other crystallographic data. Positional and thermal displacement parameters are given in Table 2. Further details on the structure determination can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein- Leopoldshafen (FAX +49

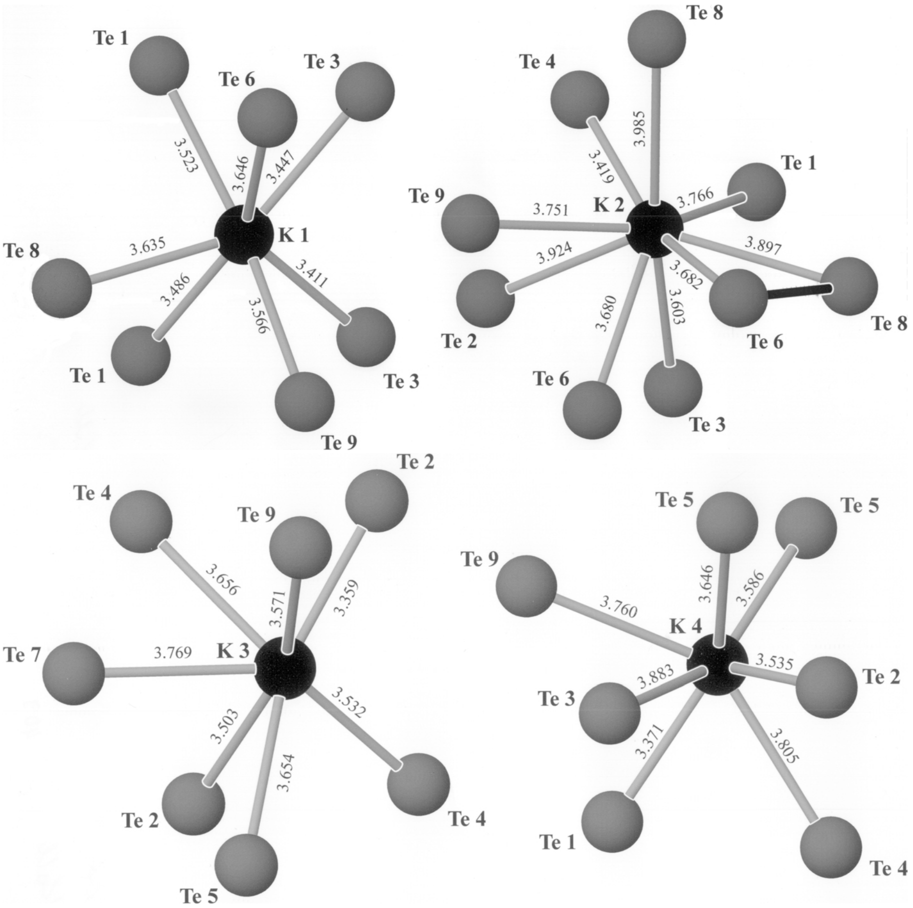

Fig. 3. Detailed views of the chalcogen coordination of the cations K1 – K4.

(0)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) under CSD 391207.

Results and Discussion

$K_4Ti_3Te_9$ crystallizes with a new structure type which is characterized by the formation of infinite anionic chains, $^1_\infty[Ti_3Te_9]^{4-}$. These chains traverse the structure in the a-direction and are packed in the sense of a hexagonal rod packing which yields triangular channels hosting the alkali cations (Fig. 1). The chains comprise three crystallographically independent Ti-atoms in their translation period, all in distorted octahedral chalcogen coordinations. The $TiTe_6$-octahedra share opposite faces, however, due to the deformation of the octahedra the resulting arrangement is not a linear but a slightly ondulated chain with Ti-Ti-Ti angles close to 166° (see Table 3). The Ti-Ti distances are close to 3.0 Å virtually ruling out any homonuclear interactions. The individual Ti—Te distances lie in the range of 2.700(3) to 2.841(3) Å, the average Ti—Te bond distance is 2.772(4) Å and is identical for all Ti-atoms within experimental errors. A slightly higher value ($d_{Ti-Te} = 2.789(2)$ Å) is found in the anionic chains of Tl_2TiTe_3 [22]. As can be seen from Fig. 2 the main reason for the distortion of the Ti—Te octahedra is the formation of two ditelluride pairs (Te(5)–Te(7)) and (Te(6)–Te(8)) which act as bidentate ligands on Ti(3) and Ti(2), respectively. Surprisingly the Te–Te bond distances (2.960(2) and 3.025(2) Å) within the pairs are distinctly larger than expected for a Te–Te single bond ($r(Te)_{cov} = 1.39$ Å).

In $K_4Ti_3Te_9$ the four crystallographically independent alkali-cations occupy the triangular channels formed by the packing. As might be expected, each of them connects three anionic chains. Due to their off centred positions and due to the severe distortions of the $TiTe_6$ octahedra their chalcogen environments are irregular. K(1) and K(3) are both in distorted monocapped trigonal prismatic coordinations (Fig. 3). The trigonal prisms are connected via common edges to build infinite corrugated chains running along [010] which in turn are connected via the ditelluride pairs yielding a layered arrangement. No proper rationalization is possible describing the coordinations of K(2) or K(4) (seven and nine Te-neighbours, respectively). Average K-Te distances are calculated as 3.644(6) Å.

The most striking feature of the present compound is certainly the presences of Te-Te pairs with exceptionally long bond distances. The application of Pauling's bond order – bond length relationship [23]

$$d_n = d_1 - 0.71 \log n$$

reveals fractional bond orders of 0.55 and 0.45 for $d_1 = 2.78$ Å which comes close to 0.5. The reduction of the bond order with respect to that of a "normal" ditelluride (Te_2^{2-}) group could be explained by the presence of one further electron occupying an antibonding level of the ditelluride unit yielding Te_2^{3-}. Neglecting weak bonding interactions between the ditelluride groups and their tellurium neighbours (the nearest homonuclear neighbours of the two pairs are at 3.215(2) and 3.333(2) Å apart) the Te_2-units might be considered as isolated groups. Under this assumption the crystal chemical formula can be rationalized as $(K^+)_4{}^1_\infty[(Ti^{4+})_3(Te_2)^{3-}{}_2(Te^{2-})_5]$. In the normal valence compound Tl_2TiTe_3 [22] which – for easier comparison – may be formulated as $Tl_6Ti_3Te_9$ a sufficient number of electrons can be supplied by the cations and homonuclear Te-Te bonding is no longer necessary.

Partial Te-Te bonds are well established in compounds containing hypervalent tellurium [24] in square planar (pseudo octahedral) coordination by its homonuclear neighbour leading to the formation of discrete Te_5^{6-} groups as for instance in Ga_2Te_5 [25], K_2SnTe_5 [26] or Re_2Te_5 [27], or polymerisation products thereof as in the infinite chains, ${}^1_\infty(Te_5)^{2-}$, of Rb_2Te_5 [28] or Cs_2Te_5 [29]. The Te-Te distances originating from the hypervalent centre are typically in the range of 2.90 – 3.03 Å. As has been stated in the introduction, similar Te-Te distances (but no square Te_5-groups) are found in many alkali polytelluromet-allates of the group IVa-metals but no attempt has so far been made to reach a rational interpretation of their occurrence. Since they show a wider spread of homonuclear bond distances, such an interpretation appears less obvious and probably would require extensive theoretical calculations, in particular for tellurium-rich compounds like $K_4Hf_3Te_{17}$ [18] where the system of partial Te-Te bonds extends over several tellurium atoms. For $K_4Ti_3Te_9$ it should be easier since only tellurium pairs need to be considered. Conductivity measurements and the determination of the magnetic susceptibility should, in addition, help to clarify the bonding situation within the $[Ti_3Te_9]^{4-}$-anions.

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[1] K. O. Klepp, Z. Naturforsch. **40b**, 229 (1985).
[2] C. Rumpf, W. Bensch, Z. Naturforsch. **55b**, 695 (2000).
[3] R. Tillinski, C. Näther, W. Bensch, Z. Kristallogr. **Suppl. 17**, 117 (2000).
[4] F. Q. Huang, J. A. Ibers, Inorg. Chem. **40**, 865 (2001).
[5] S. A. Sunshine, D. Kang, J. A. Ibers, J. Am. Chem. Soc. **109**, 6202 (1987).
[6] F. Q. Huang, J. A. Ibers, Inorg. Chem. **40**, 2346 (2001).
[7] R. Tillinski, C. Rumpf, W. Bensch, Z. Anorg. Allg. Chem. **627**, 1405 (2001).
[8] D. Kang, J. A. Ibers, Inorg. Chem. **27**, 549 (1988).
[9] J. A. Aitken, M. G. Kanatzidis, Z. Naturforsch. **56b**, 49 (2001).
[10] K. O. Klepp, A. Kolb, Z. Kristallogr. **Suppl.17**, 171 (2000).
[11] C. Rumpf, C. Näther, W. Bensch, Z. Anorg. Allg. Chem. **627**, 378 (2001).
[12] F. Q. Huang, Acta Crystallogr. **C56**, 1059 (2000).
[13] J. A. Cody, M. F. Mansuetto, M. A. Pell, S. Chien, J. A. Ibers, J. Alloys Comp. **219**, 59 (1995).
[14] K. O. Klepp, C. Kitzmüller, A. Kolb, 10. Österreichische Chemietage, Book of Abstracts, PO 10, Linz (2002).
[15] M. A. Pell, J. A. Ibers, Chem. Mat. **8**, 1386 (1996).
[16] J. A. Cody, J. A. Ibers, Inorg. Chem. **33**, 2713 (1994).
[17] B. A. Anderson, R.-J. Wang, J. Li, Acta Crystallogr. **C56**, 2 (2000).
[18] P. M. Keane, J. A. Ibers, Inorg. Chem. **30**, 1327 (1991).
[19] P. Main, S. J. Fiske, S. Hull, L. Lessinger, G. Germain, J.-P. Declercq, M. M. Woolfson: "Multan 11/82, A System of Computer Programs for the Automatic Solution

of Crystal Structures from X-Ray Diffraction Data", Univs. of York, England and Louvain, Belgium (1982).

[20] C. K. Fair: "MolEN, An Interactive Intelligent System for Crystal Structure Analysis", Enraf-Nonius, Delft, NL (1990).

[21] N. Walker, D. Stuart, Acta Crystallogr. **A39**, 158 (1983).

[22] K. O. Klepp, D. Gurtner, to be published

[23] L. Pauling, Die Natur der Chemischen Bindung, 3rd ed., Verlag Chemie, Weinheim, (1976).

[24] J. Bernstein, R. Hoffmann, Inorg. Chem. **24**, 4100 (1985).

[25] M. Julien-Pouzol, S. Jaulmes, F. Alapini, Acta Crystallogr. **B33**, 2270 (1977).

[26] B. Eisenmann, H. Schwerer, H. Schäfer, Mater. Res. Bull. **18**, 383 (1983).

[27] F. Klaiber, W. Petter, F. Hulliger, J. Solid State Chem. **46**, 112 (1983).

[28] P. Böttcher, U. Kretschmann, J. Less-Common Met. **95**, 81 (1983).

[29] P. Böttcher, U. Kretschmann, Z. Anorg. Allg. Chem. **491**, 39 (1982).