**4. Structural description of CsTe4**

The characteristic structural element are the corrugated tellurium layers running perpendicular to the a–c plane; their traces are evident in Fig. 1. The figure also shows the cations’ arrangment in tunnel-like cavities created by the Te-layer’s corrugations. Perpendicularly to the a–c plane we find a zigzag-shaped arrangement of Cs+, surrounded by eight tellurium atoms at distances of 3.86–4.05 Å, with their arrangement showing relatively low symmetry (Table 3 and Fig. 2). At 5.04 Å, the Cs–Cs distances fall into the expected range.

Furthermore, Fig. 1 shows that the shortest Te–Te distance between layers is 3.5 Å (clearly less than the van der Waals radius of 4.4 Å [8], and almost equal to the distance between adjacent tellurium chains in Rb2Te5 and Cs2Te5 [2, 3]). It follows that just like the Te chains in M2Te5 (M = Rb, Cs), the Te layers in CsTe4 cannot be regarded as isolated from each other.

The Te–Te distances within a layer span a relatively broad range (2.75–3.38 Å) with bond angles of 90°, 103° and 180° (Table 3). The anion sublattice can be described in three ways (Fig. 3):

a) If we take into account only distances of 2.70–2.92 Å, then CsTe4 is composed of angled, isolated Te82– chains (Fig. 3a). This description emphasizes the structure’s kinship with polychalcogenide chains M2Xm (M = alkali metal, alkaline earth metal, NH4+ ; X = chalcogen; m = 2–6). The great variance of distances and angles within a single CsTe4 chain and the presence of additional Te–Te distances indicates that this description cannot be fully sufficient.

b) Including only the next largest distance (3.14 Å) leads to a completely different description (Fig. 3b): now the basic building blocks are distorted T-shaped Te4–groups, linked by bridges of 2.75 and 2.76 Å into Te18 rings, which in turn combine to form a **tellurium layer**.

c) If we additionally take into account the distance of 3.38 Å (Fig. 3c), we obtain building blocks consisting of five Te each, which connect into distorted Te5-crosses with double, triple and quadruple bonds between tellurium atoms ([TecTet2Tet2/2]– with c = central, t = terminal). The resulting strands combine into a layer via double bonded atoms.

**5. Discussion**

In terms of structural chemistry, the anion sublattice of CsTe4 relates to AB3E2 compounds (BrF3, IF3; E = non-bonding electron pair) just like the anion sublattices of M2Te5 (M = Rb, Cs) compounds relate to AB4E2 compounds (BrF4–, XeF4) [2, 3]: the pseudo-trigonal bipyramidal, T-shaped Te4– group is built just like BrF3, while the pseudo-octahedral, square-planar Te52– group structurally resembles XeF4. However, both Te4– and Te52– contain fewer electrons than BrF3 and XeF4, respectively. Both building blocks characteristic of the respective solids compensate for this lack of electrons in the same way – by condensing into infinite 1D or 2D compounds, respectively, via bridges whose lengths equal the single covalent bonding distance of Te–Te.

Among M2Te5 tellurides there is a substance, namely Ga2Te5 [2, 9], whose structure contains a 36e Te56– group which is isoelectronic with XeF4 and present in the lattice as an isolated anion. On the other hand, CsTe4 is so far the only representative with a pseudo-trigonal bipyramidal building block consisting only of telluride. Notably, there is no example containing a 28e Te44– unit isoelectronic with BrF3 and present as an isolated group. Formally, alkali metal ditellurides M2Te2 = M4Te4 exhibit the desired composition. Unfortunately, the structures of comparable ditellurides are not known, the single exception being that of MgTe2 (pyrite-type [10]). Our attempts at describing Cs2Te2 [11] have so far yielded only microcrystalline products with relatively complicated powder diagrams.

As mentioned above, the anion sublattice can also be constructed based on patterns other than the T-shaped Te44– unit favored here. Thus the structure of CsTe4 becomes an example of the transition from isolated Xn2– chain segments to more highly condensed compounds of non-chain sections of cation-stabilized metallic tellurium [2, 4, 12]. In this respect LiTe3 [13] can be considered analogous to CsTe4: when regarding only the shortest Te–Te distances (2.86–3.02 Å) in LiTe3 as bonds, the tellurium sublattice consists of chains. Unlike in CsTe4, however, the latter are not short, isolated chain segments, but infinite 1D helices built from alternating linear (pseudo-trigonal bipyramidal) and angled (pseudo-tetrahedral) Te3 components. Including the next larger Te–Te distance of 3.14 Å gives rise to T-shaped units which bridge the parallel chains just described. Finally, taking into account the Te–Te distances of 3.25 and 3.32 Å results in a 3D compound composed of distorted Te5 units. However, the level of connectivity is higher in the case of LiTe3 than in that of CsTe4. The most symmetrical arrangement of tellurium atoms possible is realized in AgTe3 [4]; AgTe3 and LiTe3 are thus closely related [2, 4, 13].