**4. Structure description and discussion**

NaTe3 contains Te62– chains arranged along the c-axis of its partial anionic crystal lattice (Te–Te: 2.98 Å [twice], 2.92 Å [twice], 2.77 Å; bond angle Te–Te­­–Te: 94.7° [twice] and 97.6°; dihedral angles: ±94.6° [twice] and ±95.3°). Thus, we find relatively undisturbed chains with a structural chemistry resembling that of polysulfides and polyselenides, present in their all-trans conformation and, in accordance with space-group symmetry, appearing in equal proportions as either left or right-handed helices (signs of the dihedral angles: - - - and + + +, respectively) [Fig. 1].

Among the tellurides with comparably complex partial anion lattices, only CsTe4 [15] contains a chain-like fragment with Te–Te distances of 2.75­–2.92 Å, which presents a conformation not at all typical for chalcogenide chains Xn2–(dihedral angles: +114.4°, -73.5°, +180°, +73.5°, -114.4°). By connecting the Te82– chains in CsTe4 at their initial and terminal atoms, we obtain a two-dimensionally infinite arrangement of anions 2∞[TeTe4–].

In perfect analogy with the above, the initial and terminal atoms of the Te62– fragments in NaTe3 are located at only 3.16 Å from each other. Thus, if we regard them as bonding, the isolated Te62– chains give rise to one-dimensionally infinite strings, which allows for a very different description of the partial anion lattice: six tellurium atoms Te(3) (three initial and three terminal atoms of six chains in total) form an almost undistorted cube in which two diagonally opposite vertices remain unoccupied (Fig. 1 and 2). An additional telluride atom Te(1) is placed at each of these six telluride atoms at a distance of 2.98 Å at the exo position. No bond angle between any two of these twelve atoms in total deviates from 90° or 180°, respectively, by more than 2.5° (Table 4, Fig. 2).

This cube-like twelve-atom cluster can be assigned 78 valence electrons if we ascribe two additional non-bonding electron pairs to each of the inner six triple-bonded atoms Te(3) (pseudo-trigonal bipyramidal coordination) and also allocate two non-bonding pairs to each of the six double-bonded atoms Te(1) at the exo position (pseudo-tetrahedral coordination). Thus, the cluster can be described as Te126–. According to the composition of NaTe3 ≙ Na6Te18, six tellurium atoms Te(2) have not yet been taken into account; they act to connect the clusters within the strings 1∞[(Te126­–)(Te2)3] as three formally non-valent “handles” $⋅$ $\overbar{ Te}$–$\overbar{Te}$ $ ⋅$, also represented in Fig. 2.

Two sodium atoms placed at the free vertices complete the cube. Furthermore, each of the six inner tellurium atoms forming the cube has contact with a Te(1) atom from another string at a distance of 3.33 Å, effectively giving rise to a three-dimensional network (Fig. 3). It becomes evident that the section of the NaTe3 structure chosen in Fig. 3 is a slightly distorted image of analogous sections of the AgTe3 structure [14]. In lattices as complex as AgTe3 and the section of the NaTe3 structure presented here, assigning electrons to specific atoms is no longer meaningful, nor is it feasible using simple methods.

The basic building block recognizable in Fig. 3, a T-shaped, pseudo-trigonal bipyramidal TeTe3 group (shaded), which is usually completed to form a quadratic TeTe4 group, frequently appears in telluride structures and demonstrates the close kinship between them— It was found as quasi-isolated Te56– groups in Ga2Te5 [7] and M2SnTe5 [12] (M ≙ K, Rb) [8, 9], completed by further atoms to form a Te72– unit in Re2Te5 [12], as well as in one-dimensionally infinite chains 1∞[Te52­–] in M2Te5 (M ≙ Rb, Cs) [10, 11], and distorted within a two-dimensionally infinite layer 2∞[TeTe2Te2/2] in CsTe4 [15]; it was found also in the complex lattices of some lanthanide tellurides [13] as well as in AgTe3 [14] and LiTe3 [19], and finally in NaTe3.