

# Coordination Polyhedra $\text{BiX}_n$ ( $X = \text{S}, \text{Se}, \text{or Te}$ ) in Crystal Structures

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*Using Voronoi–Dirichlet polyhedra and the intersecting sphere method, specific features of coordination of bismuth atoms in the S-, Se-, or Te-containing compounds structure was analyzed. Stereo effect attenuation of the lone-electron pair of Bi(III) atoms was observed as the electronegativity of the surrounding atoms in a series of  $\text{BiS}_n$ – $\text{BiSe}_n$ – $\text{BiTe}_n$  complexes decreased. Impact of the central atom nature on the stereochemical activity of the lone-electron pair was analyzed through the example of certain halogen and chalcogen-containing complexes.*

**Keywords:** Voronoi–Dirichlet polyhedra, intersecting sphere method, stereo effect, bismuth, lone-electron pairs.

In crystal chemistry of compounds p-block elements with incomplete valence (arsenic, stibium, bismuth, etc.), the problem of quantitative assessment of the stereo effect of lone-electron pairs (LEP) and the nature of their impact on the central atom coordination sphere depending on its valence state, nature of the nearest neighbor atoms and other factors remains unresolved. The stereochemistry of p-block elements is distinguished by severe deformation of their coordination sphere and a wide range of atomic distances in it. Traditional crystallochemical analysis methods do not always lead to unambiguous division into the first and second coordination spheres of such atoms and determination of their coordination numbers (CN) in the crystal structure.

Previously, using, in particular, compounds containing  $\text{SbX}_n$  ( $X = \text{S}, \text{Se}, \text{Te}$ ) [1] and  $\text{BiO}_n$  [2] complexes, it was demonstrated that Voronoi–Dirichlet polyhedra (VD) and their characteristics can be used to quantify LEP information stereochemical activity. The purpose of this study was to analyze specific features of coordination of bismuth atoms in the structure of crystals containing  $\text{BiX}_n$  ( $X = \text{S}, \text{Se}, \text{or Te}$ ) coordination polyhedra.

Input crystal structure data were gathered from databases on the structure of coordination [3] and inorganic [4] compounds. Only the compounds meeting all of the following criteria were analyzed: 1) structure determination divergence factor does not exceed 10%; 2) the structure contains atoms in static arrays; 3) coordinates of all atoms, including hydrogen, are known; 4) Bi atoms are matched with  $\text{BiX}_n$  ( $X = \text{S}, \text{Se}, \text{Te}$ ) coordinator polyhedra. Data on the structure of 189 compounds met these requirements, including 268, 84, and 22 crystallographic types of Bi atoms (including 368 Bi(III) and 6 Bi(II)), where  $X = \text{S}, \text{Se}, \text{and Te}$ , respectively. TOPOS software suite [5] was used to calculate characteristics

of VD polyhedra of the atoms and perform statistical processing of the results. The intersecting sphere method was used to determine the atoms CN [6]. As an example, Table 1 shows calculation results for some of the analyzed structures, Table 2 shows final characteristics of VD polyhedra of Bi atoms. A full list of the studied compounds is available upon request at [pushkin@samsu.ru](mailto:pushkin@samsu.ru).

For all 368 crystallographic types of Bi(III) atoms, VD polyhedra had from 6 to 21 faces with the average of  $N_f = 14(3)$  for  $X = \text{S}, \text{Se}$ , and  $13(2)$  for  $X = \text{Te}$ . As the number of neighbor atoms of a certain central atom corresponds to the number of faces of its VD polyhedron, we can conclude that, in the structures under study, Bi(III) atoms with CN from 3 to 8 have between 6 and 21 neighbor atoms. In most cases, apart from sulfur, selenium, or tellurium, VD polyhedra of Bi(III) atoms contain atoms of a number of other elements.

Despite the varying CN of Bi atoms and the variety of VD polyhedra shapes in the structure of the compounds in question, there is a correlation between solid angles  $\Omega$  of VD polyhedra faces and  $r(\text{Bi-X})$  distances. According to OLS, both valence and non-valence interactions in the coordination sphere of Bi atoms can be described by the following linear functions:

$$\Omega(\text{Bi-S}) = 38.4(2) - 8.38(6)r(\text{Bi-S}) \quad (1)$$

$$\{\rho = -0.957, 2070 \text{ contacts Bi-S}\};$$

$$\Omega(\text{Bi-Se}) = 40.5(3) - 8.48(9)r(\text{Bi-Se}) \quad (2)$$

$$\{\rho = -0.963, 657 \text{ contacts Bi-Se}\};$$

$$\Omega(\text{Bi-Te}) = 45.9(7) - 9.4(2)r(\text{Bi-Te}) \quad (3)$$

$$\{\rho = -0.967, 138 \text{ contacts Bi-Te}\}.$$

As an example, Fig. 1 shows the  $\Omega(r)$  dependency for  $\text{BiS}_n$  complexes (for selenium- and tellurium-containing structures, charts were similar). The points corresponding to 2070 contacts Bi-S form a

Table 1

## Properties of bismuth atoms neighbors in structures of certain compounds

Bi atom VD polyhedron*			Overlap volume ( $\text{\AA}^3$ ) of two spheres with radii**				Bi-X overlap type
X neighbor atom	$r(\text{Bi-X}), \text{\AA}$	$\Omega(\text{Bi-X}), \%$	$r_s \times r_s$	$r_s \times R_{sd}$	$R_{sd} \times r_s$	$R_{sd} \times R_{sd}$	
Structure of $\text{Bi}_2\text{S}_3$ {89323} Bi(2)=Bi(III) with CN = 7							
S(3)	2,583	16,94	0	1,7854	0,0596	2,6078	$P_3$
S(2)	2,737( $\times 2$ )	16,22( $\times 2$ )	0	1,3017	0	2,0110	$P_2(\times 2)$
S(3)	2,955( $\times 2$ )	13,66( $\times 2$ )	0	0,5891	0	1,0795	$P_2(\times 2)$
S(1)	3,311( $\times 2$ )	9,69( $\times 2$ )	0	0,0440	0	0,2258	$P_2(\times 2)$
Bi(2)	3,971( $\times 2$ )	0,22( $\times 2$ )	0	0	0	0	$P_0(\times 2)$
S(2)	4,041	3,15	0	0	0	0	$P_0$
Bi(1)	4,329	<0,01	0	0	0	0	$P_0$
S(1)	4,556	<0,01	0	0	0	0	$P_0$
Structure of $\text{TlBiS}_2$ {172572} Bi(1)=Bi(III) with CN=6							
S(1)	2,832( $\times 6$ )	16,67( $\times 6$ )	0	0,9640	0	1,5850	$P_2(\times 6)$
Structure of $\text{Bi}_2\text{Al}_4\text{S}_8$ {408439} Bi(1)=Bi(II) with CN=5							
S(1)	2,844( $\times 4$ )	16,11( $\times 4$ )	0	0,9084	0,0007	1,9923	$P_3(\times 4)$
Bi(1)	3,135	12,87	0,0105	0,2800	0,2800	0,9629	$P_4$
Al(1)	4,000( $\times 4$ )	0,27( $\times 4$ )	0	0	0	0	$P_0(\times 4)$
S(1)	4,015( $\times 4$ )	4,52( $\times 4$ )	0	0	0	0	$P_0(\times 4)$
Al(2)	4,061( $\times 4$ )	0,17( $\times 4$ )	0	0	0	0	$P_0(\times 4)$
S(1)	4,168( $\times 4$ )	0,71( $\times 4$ )	0	0	0	0	$P_0(\times 4)$
Structure of $\text{Bi}[\text{N}((\text{C}_3\text{H}_7)_2\text{P}\text{Te})_2]_3$ {TASJON} Bi(1)=Bi(III) with CN=6							
Te(2)	Te(2)	Te(2)	Te(2)	Te(2)	Te(2)	Te(2)	Te(2)
Te(3)	Te(3)	Te(3)	Te(3)	Te(3)	Te(3)	Te(3)	Te(3)
Te(1)	Te(1)	Te(1)	Te(1)	Te(1)	Te(1)	Te(1)	Te(1)
H(25)	H(25)	H(25)	H(25)	H(25)	H(25)	H(25)	H(25)
H(11)	H(11)	H(11)	H(11)	H(11)	H(11)	H(11)	H(11)
H(32)	H(32)	H(32)	H(32)	H(32)	H(32)	H(32)	H(32)
H(9)	H(9)	H(9)	H(9)	H(9)	H(9)	H(9)	H(9)

Notes:

\*  $r(\text{Bi-X})$  is the atomic distance,  $\Omega(\text{Bi-X})$  is the solid angle in per cent of  $4\pi$  sr under which the face shared by VD polyhedra of Bi and X atoms is visible from the nuclei of any of them. Values in brackets indicate the number of symmetrical-equal atomic distances, corresponding solid angles of VD polyhedra faces and pair overlap types. Values in curly brackets indicate database codes of each compound [3, 4].

\*\* In all products, the respective bismuth atom radius comes first, followed by the X neighbor atom,  $r_s$  is the Slater radius of the corresponding atom. Zero means that the respective spheres do not overlap.

single sequence, making it impossible to delineate valence and non-valence contacts by considering only atomic distances or solid angles, and, therefore, to determine the Bi atoms CN accurately from the perspective of traditional crystal chemistry.

According to the obtained data (Table 2), Bi(III) atoms CN varies between 3 and 8 for  $X = \text{S}$ , Se (there are no compounds with  $\text{CN}_{\text{Bi}} = 4$  in selenides), while for  $X = \text{Te}$ , only CN of 6 and 7 are observed, with prevalence of CN 6. Coordination

Table 2

Properties of bismuth atoms VD polyhedra surrounded by sulfur, selenium, and tellurium atoms\*

Complex	CN	Number of atoms	N <sub>f</sub>	N <sub>nb</sub>	R <sub>sp</sub> , Å	V <sub>vdp</sub> , Å <sup>3</sup>	D <sub>A'</sub> , Å	A <sub>ns</sub>	G <sub>3</sub>	r(Bi-X), Å		μ
										range	average	
Bi(II)S <sub>n</sub>	5	2	21(0)	3,2	1,862(1)	27,02(5)	0,185(8)	0,099	0,0841(1)	2,841-2,844	2,843(1)	8
										3,135-3,144**	3,140(7)**	
Bi(III)S <sub>n</sub>	3	7	18(2)	5,0	1,76(4)	23(2)	0,24(6)	0,136	0,084(2)	2,53-2,64	2,58(3)	21
	4	5	18(3)	3,5	1,77(2)	23,3(9)	0,29(5)	0,164	0,084(1)	2,54-3,19	2,71(23)	20
	5	36	15(2)	2,0	1,78(2)	23,5(7)	0,22(5)	1,124	0,0838(8)	2,46-3,19	2,81(20)	180
	6	137	14(3)	1,3	1,76(2)	22,8(8)	0,14(8)	0,080	0,084(1)	2,45-3,22	2,84(16)	822
	7	68	13(1)	0,9	1,74(3)	22(1)	0,16(4)	0,092	0,0835(9)	2,56-3,36	2,91(20)	476
	8	13	13(1)	0,6	1,73(2)	21,6(8)	0,11(3)	0,064	0,0818(5)	2,62-3,29	2,95(18)	104
	all	266	14(3)	-	1,76(3)	23(1)	0,16(7)	0,091	0,084(1)	2,45-3,36	2,86(18)	1623
	Bi(II)Se <sub>n</sub>	5	2	21	3,2	1,922(5)	29,8(2)	0,19(1)	0,099	0,0838(1)	2,95-2,97 3,14-3,15**	2,959(7) 3,143(7)**
Bi(III)Se <sub>n</sub>	3	2	21(1)	6,0	1,838(2)	26,03(8)	0,232(7)	0,126	0,0839(2)	2,66-2,72	2,70(2)	6
	5	10	13(2)	1,6	1,86(2)	26,9(7)	0,25(4)	0,134	0,0840(6)	2,67-3,27	2,9(2)	50
	6	62	13(3)	1,2	1,83(1)	25,8(6)	0,09(7)	0,049	0,0834(8)	2,65-3,46	3,0(2)	372
	7	4	13,0(8)	0,9	1,818(3)	25,2(1)	0,16(4)	0,088	0,0815(5)	2,75-3,39	3,1(2)	28
	7***	2	17	1,4	1,98(1)	32,5(7)	0,40(3)	0,202	0,0879(6)	2,655-2,658 3,75-4,05****	2,657(2) 4,0(1)****	6
Bi(III)Te <sub>n</sub>	8	2	13,5(7)	0,7	1,811(6)	24,9(2)	0,174(6)	0,096	0,0818(3)	2,76-3,49	3,1(2)	16
	all	82	14(3)	-	1,84(3)	26(1)	0,12(9)	0,065	0,083(1)	2,65-3,48	3,0(2)	478
Bi(II)Te <sub>n</sub>	6	2	13,5(7)	1,3	1,997(7)	33,4(4)	0,06(5)	0,030	0,0831(1)	3,04-3,50 3,238**	3,2(2) 3,238**	10
	6	19	12(1)	1,0	1,97(2)	32(1)	0,04(3)	0,020	0,0833(8)	2,97-3,40	3,2(1)	114
Bi(III)Te <sub>n</sub>	7***	1	17	1,4	2,09	38,5	0,36	0,172	0,0863	2,883 3,94-4,21****	2,883 4,1(1)****	3
	all	20	13(2)	-	1,97(4)	32(2)	0,06(8)	0,030	0,083(1)	2,88-3,40	3,2(1)	117

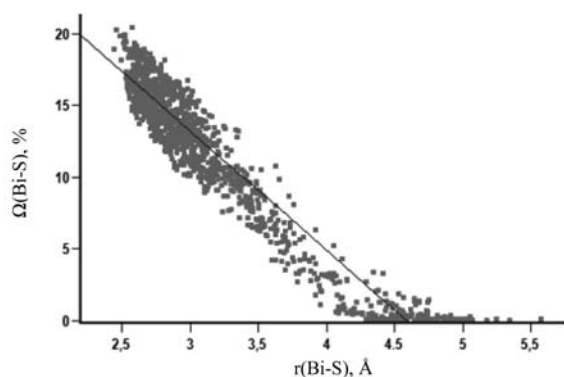
Notes:

\* Specified for each type of bismuth atoms: CN is the coordination number; N<sub>nb</sub> is the average number of non-valence contacts Bi...Z, per one Bi-X bond (X = S, Se, Te); RSD is the radius of the sphere with the volume of V<sub>vdp</sub>; V<sub>vdp</sub> is the VD polyhedron volume; D<sub>A'</sub> is the Bi atom nucleus displacement from the geometrical center of gravity of its VD polyhedron; A<sub>ns</sub> is the ratio D<sub>A'</sub>/R<sub>sp</sub>; G<sub>3</sub> is the unitless value of the second moments of inertia of the VD polyhedron; r(Bi-X) is the length of Bi-X bonds in a traditional coordination polyhedron with a specific CN; μ is the number of such bonds. Mean square deviations are provided in brackets.

\*\* r(Bi-Bi) is the Bi-Bi bond length.

\*\*\* Only appears in the structures of K<sub>3</sub>BiSe<sub>3</sub>, RbK<sub>2</sub>BiSe<sub>3</sub>, K<sub>3</sub>BiTe<sub>3</sub>, and corresponds to 3P<sub>4</sub>(Bi<sup>III</sup>-Se) + 1P<sub>3</sub>(Bi<sup>III</sup>-K) + 3P<sub>3</sub>(Bi<sup>III</sup>-K(Rb)) coordination for K<sub>3</sub>BiSe<sub>3</sub>, RbK<sub>2</sub>BiSe<sub>3</sub> and 3P<sub>4</sub>(Bi<sup>III</sup>-Te) + 4P<sub>3</sub>(Bi<sup>III</sup>-K) coordination for K<sub>3</sub>BiTe<sub>3</sub>.

\*\*\*\* r(Bi-K(Rb)) is the Bi-K(Rb) bond length.



**Fig. 1.**  $\Omega(r)$  dependency for Voronoi-Dirichlet polyhedra of Bi atoms.

polyhedra of Bi(III) atoms predominantly consist of chalcogen atoms. The analysis showed that, in the structure of three compounds ( $K_3BiSe_3$  {78841},  $RbK_2BiSe_3$  {85412},  $K_3BiTe_3$  {300183}), bismuth (III) atoms form additional valence contacts with atoms of metals Q (Q = K or Rb), increasing the CN of Bi(III) atoms as compared to the origin data. As per the intersecting sphere method, CN Bi(III) atoms in the said compounds is 7, however, the coordination polyhedron of bismuth atoms contains, apart from three Se (or Te) atoms, four atoms of alkali metals (K or Rb), therefore,  $_{Bi} CN = 7$  (Table 3). With respect to Q metal atoms, Bi(III) atoms show CN = 4, forming a scaffold structure consisting of bismuth and potassium (or rubidium) atoms. These structures have abnormally high values of  $V_{VDP}$  of

bismuth atoms ( $32.5(7) \text{ \AA}^3$  as compared to the average of  $26(1) \text{ \AA}^3$  for  $K_3BiSe_3$ ,  $RbK_2BiSe_3$ , and  $38.5 \text{ \AA}^3$  as compared to the average of  $32(2) \text{ \AA}^3$  for  $K_3BiTe_3$ ). It should be noted that the shortest distances  $r(Bi-Q)$  are within the range between the sum of Slater-type and atomic radii of Bi and Q [7]. This makes it impossible to view bismuth atoms as linked to chalcogen atoms only, resulting in a significant increase of their  $V_{VDP}$ .

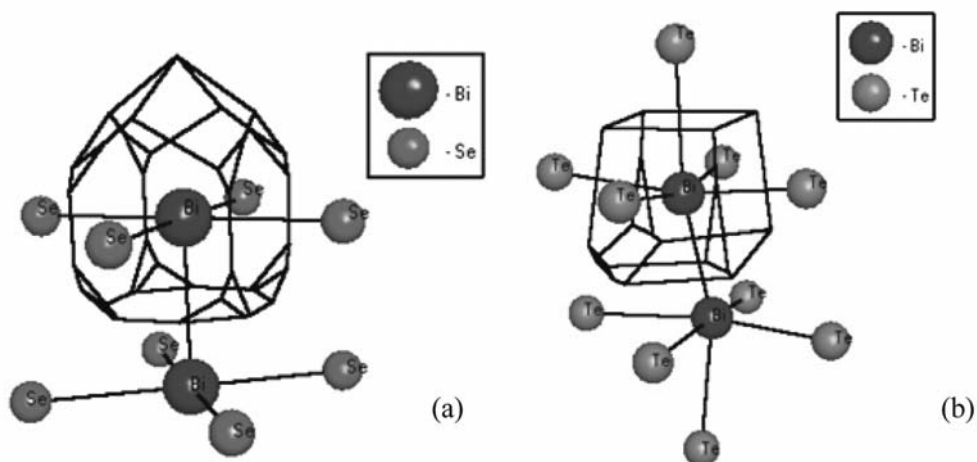
In the analyzed compounds, VD polyhedra of bismuth atoms contained 5142 faces, among which 986 faces were corresponding to Bi...Bi interactions (629, 242, and 115 for X = S, Se, and Te, respectively). The studied series included 5 compounds with Bi(II) oxidation degree:  $Bi_2Al_4S_8$  {408439} and  $Bi_2Ga_4S_8$  {408441},  $Bi_2Al_4Se_8$  {408440} and  $Bi_2Ga_4Se_8$  {408442},  $CsBi_4Te_6$  {170576}, which showed a strong chemical Bi-Bi interaction. The intersecting sphere method (Table 1) proves the presence of a valence  $Bi^{II}\text{---}Bi^{II}$  interaction ( $P_4$  type overlap in sulfides and selenides, and  $P_3$  type overlap in telluride structure). Bi(II) atoms surrounded by sulfur and selenium have CN = 5, and 6 when surrounded by tellurium. In case of sulfides and selenides, Bi atoms are squared by chalcogen atoms and form dimers with a Bi-Bi bond (Fig. 2a). In  $CsBi_4Te_6$  compound, bismuth atoms also form Bi-Bi dimers and are surrounded by tellurium atoms forming a quadrangular pyramid (Fig. 2b).

For the other  $Bi^{III}\text{---}Bi^{III}$  contacts, the distance between atoms varies between 3.32 and 4.91 Å with the average of  $4.2(3) \text{ \AA}$ , which is much higher than the shortest distances in metal bismuth, and the solid angles of the respective VD polyhedra faces

Table 3

Some properties of Bi-Q valence interactions (Q is a metal)

Q atoms	Sum of Bi and Q atom radii, Å [7]	Sum of Bi and Q Slater radii, Å [7]	Properties of the established Bi-Q bonds			Bi atom CN in relation to the Q atom	Dimension of the fragment containing bound atoms of Bi and Q	Compound formula
			$r(Bi-Q)$ , Å	$\Omega(Bi-Q)$ , %	Overlap type			
Rb	4,30	3,95	4,053 × 3	5,70 × 3	$P_2$	3	3	$RbK_2BiSe_3$
			3,763	2,78	$P_3$	1		
K	4,18	3,80	3,754	2,85	$P_3$	4	3	$K_3BiSe_3$
			3,992 × 3	5,56 × 3	$P_2$			
			3,943	3,47	$P_2$	4	3	$K_3BiTe_3$
			4,212 × 3	5,42 × 3				



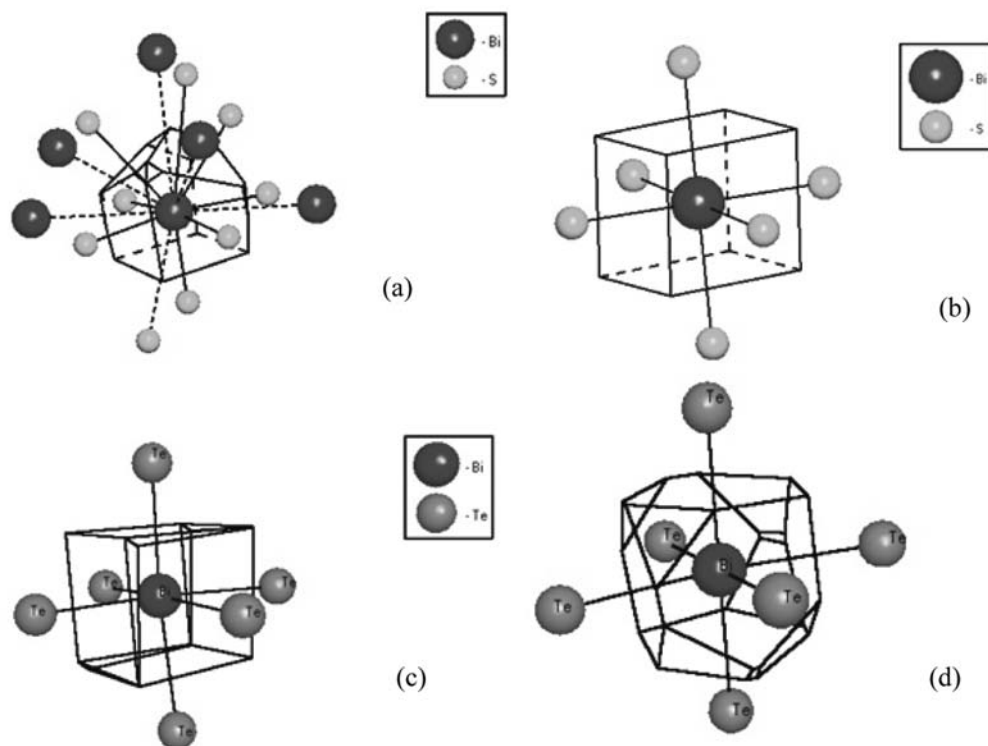
**Fig. 2.** Voronoi-Dirichlet polyhedra of Bi(II) atoms in  $\text{Bi}_2\text{Al}_4\text{Se}_8$  (a) and  $\text{CsBi}_4\text{Te}_6$  (b) structures.

$\Omega(\text{Bi}\cdots\text{Bi}) \leq 7.8\%$  (with the average of  $0.5(7)\%$ ). The same  $\text{Bi}\cdots\text{Bi}$  interactions correspond to lower correlation ratios of dependencies between solid angles  $\Omega$  of VD polyhedra faces and distances  $r(\text{Bi}\cdots\text{Bi})$  of type (1-3) ( $\rho = -0.427, -0.286$  and  $-0.780$  for  $X = \text{S}, \text{Se}$  and  $\text{Te}$ , respectively), which proves the absence of strong  $\text{Bi}^{\text{III}}\text{-Bi}^{\text{III}}$  chemical interactions in the structure of the studied compounds.

In  $\text{Bi}^{\text{III}}\text{X}_n$  complexes, with almost any CN, there is a severe distortion of VD polyhedra, making it hard to assign a specific shape to them. As an example, Fig. 3a (Table 1) shows a VD polyhedron of a Bi(2) atom with CN 7 in the structure of  $\text{Bi}_2\text{S}_3$ . Only in some cases, such as in  $\text{TlBiS}_2$  compound (Fig. 3b), Bi(III) atoms with CN 6 form VD polyhedra as slightly deformed cubes without additional faces. In the compounds under study, VD polyhedra of Bi(III) atoms with CN 6 surrounded by tellurium atoms were close to a cube with small additional faces (as an example, Fig. 3c shows the structure of  $\text{Bi}_2\text{Te}_3$  {184631}. This is hardly surprising, as the VD polyhedron is a polygon dual to the coordination polyhedron shaped like a slightly deformed octahedron for a Bi(III) atom with this CN. The only exception is the  $\text{Bi}[\text{N}((\text{C}_3\text{H}_7)_2\text{P}\text{Te})_2]_3$  compound {TASJON} containing solid organic ligands (Fig. 3d, Table 1). In this structure, VD polyhedra of bismuth atoms have 8 additional faces corresponding to non-valence contacts  $\text{Bi}\cdots\text{H}$ . These faces have long atomic distances  $r(\text{Bi}\cdots\text{H}) > 3.812 \text{ \AA}$  and small solid angles  $\Omega(\text{Bi}\cdots\text{H}) < 4.27\%$  ( $\Omega$  are specified in per cent of the full solid angle of  $4\pi \text{ sr}$ ). In total, about 20 % of the total solid angle is attributable to non-valence interactions  $\text{Bi}\cdots\text{H}$ . In the intersecting sphere method, such contacts correspond to  $P_0$  intersections and are van der Waals interactions.

As per Table 2, as the CNs of Bi(III) atoms increase, average atomic distance  $r(\text{Bi(III)}\text{-X})$  generally increases accordingly, symbolically with a reduction in the number of non-valence contacts per one Bi-X bond ( $N_{\text{nb}}$ ). At the same time, the radius of the spheric domain ( $R_{\text{sd}}$ ) the volume of which is equal to that of the VD polyhedron ( $V_{\text{VDP}}$ ) of the same atom can be considered constant within the triple error tolerance for neighbor X atoms of a specified nature. Therefore, the size of a Bi(III) atom surrounded by chalcogens remains the same, which, according to the stereo-atomic structural model of crystalline substances, makes it possible to model bismuth atoms as “soft”, deformable spheres of constant volume.

The deformation degree of the coordination sphere of Bi atoms can be assessed by the following parameters:  $G_3$  is a unitless parameter specifying the VD polyhedron sphericity degree [8], and  $D_A$  is the value describing the nucleus displacement from the center of gravity of its VD polyhedron [9]. These parameters of Bi atoms surrounded by sulfur, selenium, and tellurium are shown in Table 2. For Bi(III) atoms, regardless of their CN and nature of neighbor atoms,  $D_A > 0 \text{ \AA}$  ( $0.16(7)$  and  $0.12(9) \text{ \AA}$  on average for  $X = \text{S}$  and  $\text{Se}$ ). Since most Bi(III) atoms in tellurides have CN = 6 (the coordination polyhedron is predominantly an almost regular octahedron) with  $D_A = 0.04(3) \approx 0 \text{ \AA}$  (except for one compound  $\text{K}_3\text{BiTe}_3$  with  $D_A = 0.36 \text{ \AA}$ ), the average value of  $D_A$  is comparatively low and amounts to  $0.06(8) \text{ \AA}$ . Displacement of Bi atoms from their VD polyhedra centers of gravity due to anisotropic distribution of electron density around the nuclei of Bi(III) atoms caused by the impact of localized LEP on bismuth atoms. As CN of Bi(III) atoms increase,



**Fig. 3.** Voronoi-Dirichlet polyhedra of Bi(III) atoms in structures:  $\text{Bi}_2\text{S}_3$  (a),  $\text{TlBiS}_2$  (b),  $\text{Bi}_2\text{Te}_3$  (c),  $\text{Bi}[\text{N}((\text{C}_3\text{H}_7)_2\text{PTe})_2]_3$  (d).

Table 4

**Properties of Bi(III) atoms VD polyhedra surrounded by oxygen [2], sulfur, selenium, and tellurium atoms\***

Complex	CN	Number of atoms	$N_f$	$R_{SD}, \text{\AA}$	$V_{VDP}, \text{\AA}^3$	$D_A, \text{\AA}$	$G_3$	$r(\text{Bi-X}), \text{\AA}$	$\mu$
$\text{Bi(III)O}_n$	3-10	220	13(2)	1.52(6)	15(2)	0.3(1)	0.088(5)	2.46(27)	1415
$\text{Bi(III)Sn}$	3-8	266	14(3)	1.76(3)	23(1)	0.16(7)	0.084(1)	2.86(18)	1623
$\text{Bi(III)Se}_n$	3.5-8	82	14(3)	1.84(3)	26(1)	0.12(9)	0.083(1)	3.0(2)	478
$\text{Bi(III)Te}_n$	6-7	20	13(2)	1.97(4)	32(2)	0.06(8)	0.083(1)	3.2(1)	117

\* The legend is the same as for Table 2.

$G_3$  generally decreases accordingly, indicating a more uniform surrounding of bismuth atoms by S, Se, and Te atoms. This is due to gradual LEP delocalization and attenuation of its stereochemical activity associated with the CN increase.

Let us compare reach characteristics of bismuth atoms in  $\text{BiO}_n$  [2] and  $\text{BiX}_n$  complexes ( $X = \text{S}, \text{Se}, \text{Te}$ ). As complexes transition from  $\text{Bi(III)O}_n$  to  $\text{Bi(III)X}_n$  ( $X = \text{S}, \text{Se}, \text{Te}$ ) (Table 4), the average atomic distance  $\text{Bi(III)-X}$  increases accordingly (2.46(27), 2.86(18), 3.0(2), 3.2(1)  $\text{\AA}$  for  $X = \text{O}, \text{S}, \text{Se}, \text{Te}$ , respec-

tively), accompanied by an increase of  $R_{SD}$  (from 1.52(6) to 1.97(4)  $\text{\AA}$ ). At the same time, the value of  $D_A$  of VD polyhedra of bismuth atoms decreases significantly (from 0.3(1) to 0.06(8)  $\text{\AA}$ ), indicating attenuation of the stereochemical activity of Bi(III) atom LEP due to a change in the nature of X neighbor atoms.

Table 4 shows an expected decrease of  $G_3$  in a number of complexes  $\text{Bi}^{\text{III}}\text{O}_n$ - $\text{Bi}^{\text{III}}\text{S}_n$ - $\text{Bi}^{\text{III}}\text{Se}_n$ - $\text{Bi}^{\text{III}}\text{Te}_n$  (from 0.088(5) to 0.083(1)) and the central atom neighbors becoming more uniform as the electro-

Table 5

Some properties of VD polyhedra of A atoms in complexes AX<sub>n</sub>z- (A = Tl, Bi, Sn, Pb, Sb, As, Cl, S, Se, Te, where X = halogen or chalcogen)

Complex	CN	D <sub>A</sub> , Å	R <sub>SD</sub> , Å	G <sub>3</sub>	A <sub>ns</sub> = D <sub>A</sub> /R <sub>SD</sub>	References
Tl <sup>I</sup> O <sub>n</sub>	3–12	0,20	1,79	0,083	0,112	[15]
Sn <sup>II</sup> O <sub>n</sub>	3–6	0,50	1,66	0,093	0,301	[16]
Sn <sup>II</sup> F <sub>n</sub>	3–6	0,50	1,63	0,095	0,307	[10]
Sn <sup>II</sup> Cl <sub>n</sub>	3–6	0,30	1,82	0,086	0,165	
Sn <sup>II</sup> Br <sub>n</sub>	3–5	0,23	1,86	0,084	0,124	
Sn <sup>II</sup> I <sub>n</sub>	3–6	0,11	1,96	0,083	0,056	
Pb <sup>II</sup> O <sub>n</sub>	3–12	0,20	1,62	0,085	0,123	[17]
Pb <sup>II</sup> F <sub>n</sub>	5–10	0,10	1,53	0,082	0,065	[18]
Pb <sup>II</sup> Cl <sub>n</sub>	6–8	0,07	1,78	0,082	0,039	
Pb <sup>II</sup> Br <sub>n</sub>	4–8	0,08	1,87	0,083	0,043	
Pb <sup>II</sup> I <sub>n</sub>	4–7	0,06	1,98	0,082	0,030	
As <sup>III</sup> O <sub>n</sub>	3–5	0,61	1,54	0,104	0,396	[19]
As <sup>III</sup> F <sub>n</sub>	3–5	0,56	1,44	0,102	0,389	[11]
As <sup>III</sup> Cl <sub>n</sub>	3–6	0,30	1,64	0,090	0,183	
As <sup>III</sup> Br <sub>n</sub>	3–6	0,20	1,71	0,087	0,117	
As <sup>III</sup> I <sub>n</sub>	3–6	0,15	1,81	0,085	0,083	
Sb <sup>III</sup> O <sub>n</sub>	3–9	0,50	1,57	0,098	0,318	[20]
Sb <sup>III</sup> S <sub>n</sub>	3–6	0,31	1,77	0,086	0,175	[1]
Sb <sup>III</sup> Se <sub>n</sub>	3–6	0,27	1,83	0,085	0,148	
Sb <sup>III</sup> Te <sub>n</sub>	3–7	0,1	1,93	0,084	0,052	
Sb <sup>III</sup> F <sub>n</sub>	5–9	0,40	1,45	0,092	0,276	[12]
Sb <sup>III</sup> Cl <sub>n</sub>	3–6	0,31	1,71	0,087	0,181	
Sb <sup>III</sup> Br <sub>n</sub>	3–6	0,23	1,77	0,085	0,130	
Sb <sup>III</sup> I <sub>n</sub>	3–6	0,18	1,91	0,084	0,094	
Bi <sup>III</sup> O <sub>n</sub>	3–10	0,30	1,52	0,088	0,197	[2]
Bi <sup>III</sup> S <sub>n</sub>	3–8	0,16	1,76	0,084	0,091	This study
Bi <sup>III</sup> Se <sub>n</sub>	3,5–8	0,12	1,84	0,083	0,065	
Bi <sup>III</sup> Te <sub>n</sub>	6–7	0,06	1,97	0,083	0,030	
Bi <sup>III</sup> F <sub>n</sub>	6–9	0,10	1,41	0,084	0,071	[13]
Bi <sup>III</sup> Cl <sub>n</sub>	4–8	0,12	1,69	0,084	0,071	[14]
Bi <sup>III</sup> Br <sub>n</sub>	5–8	0,09	1,78	0,084	0,051	
Bi <sup>III</sup> I <sub>n</sub>	6	0,07	1,92	0,084	0,036	
Cl <sup>III</sup> O <sub>n</sub>	2	0,5	1,60	0,099	0,313	[21]
S <sup>IV</sup> O <sub>n</sub>	3	0,67	1,24	0,115	0,540	[22]
Se <sup>IV</sup> O <sub>n</sub>	3	0,56	1,47	0,104	0,381	[23]
Te <sup>IV</sup> O <sub>n</sub>	3–7	0,50	1,50	0,098	0,333	[24]
Cl <sup>IV</sup> O <sub>n</sub>	3	0,55	1,34	0,110	0,410	[21]

\* The legend is the same as for Table 2.

negativity of X neighbor atoms decreases. The abnormality of  $G_3$  change for  $\text{Bi}^{\text{III}}\text{X}_n$  polyhedra (decreasing rather than increasing as Bi-X bonds become more covalent) is due to the impact of LEP of Bi(III) atoms. The stereo effect of bismuth atoms LEP (in particular,  $D_A$  rise) increases as the electronegativity of X atoms rises and manifests itself most clearly in  $\text{Bi}^{\text{III}}\text{O}_n$  complexes, which is why the first coordination sphere of Bi(III) atoms is deformed significantly.

Finally, let us consider the impact of the nature of the central atom on the LEP stereo effect using the example of halide [10-14] and chalcogenide [1, 2, 15-24] complexes of  $\text{AX}_n^z$ . To disregard different radii of the central atom spherical domains, we compared only CN-averaged unitless parameters of VD polyhedra, namely,  $G_3$  and the noncentrosymmetry factor of the central atom surrounding  $A_{\text{ns}}$  calculated as  $D_A/R_{\text{SD}}$  (Table 5).

Analysis of the available data showed a linear dependency  $G_3(A_{\text{ns}})$  that can be described by the following equation:

$$G_3 = 0.061(2)A_{\text{ns}} + 0.0786(7) \quad (4)$$

with correlation coefficient  $\rho = 0.964$  (Fig. 4).

The higher the value of  $A_{\text{ns}}$  is, the more prominent the LEP stereo effect is, which leads to a deviation of the VD polyhedron from a spherical shape, and, therefore, to less uniform neighbors of the central atom and higher  $G_3$ . Further, a reduction of the E-pair stereo effect where  $D_A \rightarrow 0$  and in the limit of  $A_{\text{ns}} = 0$ , leads to  $G_3 = 0.0786(7)$  (according to equation (4)), which, within the double error tolerance, is consistent with  $G_3 = 0.077$  for a sphere. Finally, the atom E-pair stereo effect is the most prominent for the points concentrated in the upper right part of the diagram. Based on the obtained data, the stereochemical activity of LEP is most pronounced for S(IV) atoms surrounded by oxygen, and least pronounced for  $\text{Pb}^{\text{II}}\text{I}_n$ ,  $\text{Bi}^{\text{III}}\text{I}_n$ , and  $\text{Bi}^{\text{III}}\text{Te}_n$  complexes.

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