New representative of Bi_9^{5+}-containing phases: synthesis and crystal structure of the Nb^{IV}-containing $Bi_{10}Nb_3Cl_{18}$ compound

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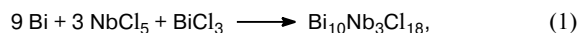*S-100 44 Stockholm, Sweden.*
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The $Bi_{10}Nb_3Cl_{18}$ compound was prepared using the high-temperature ampoule method, and its crystal structure was determined by single-crystal X-ray diffraction. This phase contains the Bi_9^{5+} cluster polycations and Bi^+ cations surrounded by the $NbCl_6^{2-}$ complex anions. The latter contain the paramagnetic central Nb^{IV} ions, as evidenced by magnetic measurements.

Key words: clusters, bismuth polycations, subhalides.

Naked ionic clusters of main-group elements occupy a significant place in cluster chemistry. Prominent representatives of such clusters are bismuth polycations, *viz.*, polyhedral positively charged ions consisting of several bismuth atoms. In the crystalline phases, the Bi_5^{3+} (trigonal bipyramid),[1] Bi_8^{2+} (square antiprism),[2—4] Bi_9^{5+} (tricapped trigonal prism),[3,5—8] Bi_6^{2+} (distorted octahedron), and Bi_5^+ (square pyramid)[9] polycations have been reported. All these ions were found in either binary lower halides of bismuth or mixed ternary halides of bismuth and another metal.

The Bi_9^{5+} polycation was found in phases of two types: 1) binary lower halides Bi_6X_7 (X = Cl or Br)[3,6] whose crystal-chemical formula can be written as $[Bi_9^{5+}(Bi_3X_{14})^{5-}]$ and 2) ternary phases $Bi_{10}M_3X_{18}$ (M = Zr or Hf; X = Cl or Br)[5,7,8] of the crystal-chemical formula $[Bi_9^{5+}Bi^+(MX_6^{2-})_3]$. As can be seen from these formulas, the polycations in the crystal lattice are stabilized by derivatives of metal halides serving as counterions. Besides, phases of the second type contain additional Bi^+ cations. The $Bi_9In_{3.67}Cl_{16}$ compound[8] has a structural motif similar to that observed in the $Bi_{10}M_3X_{18}$ phases although the former compound is devoid of Bi^+.

In the present study, we describe a new compound with composition $Bi_{10}Nb_3Cl_{18}$ belonging to phases of the second type. This compound can be prepared by either the reaction

$$9\,Bi + 3\,NbCl_5 + BiCl_3 \longrightarrow Bi_{10}Nb_3Cl_{18}, \qquad (1)$$

or the reaction

$$4\,Bi + 3\,Nb + 6\,BiCl_3 \longrightarrow Bi_{10}Nb_3Cl_{18}. \qquad (2)$$

Experimental

Synthesis of decabismuth tris(hexachloroniobate)(iv), $Bi_{10}Nb_3Cl_{18}$. The syntheses were carried out with the use of commercial Bi (99.999%) and Nb (99.98%) metals. The corresponding anhydrous chlorides $BiCl_3$ and $NbCl_5$ were prepared according to a known procedure.[10] The $Bi_{10}Nb_3Cl_{18}$ compound was prepared by reactions (1) and (2).

Weighed samples of the starting compounds (total weight was ~0.7—0.8 g per sample) corresponding to the stoichiometries of reactions (1) and (2) were placed in dried quartz ampoules, which were then evacuated and sealed. The samples were annealed at 550 °C for 7 days (reaction (1)) or for 30 days (reaction (2)) and then slowly (~5—7 K h^{-1}) cooled to ~20 °C. Reaction (1) is best suited to the preparation of polycrystalline samples, whereas reaction (2) afforded (along with impurities of the starting compounds) single crystals of $Bi_{10}Nb_3Cl_{18}$ (dark needles or elongated well-faceted bricks), which are more suitable for X-ray diffraction analysis. Both the starting anhydrous halides and the reaction product are very moisture-sensitive. Besides, the $Bi_{10}Nb_3Cl_{18}$ appeared to be sensitive to oxygen. Therefore, all operations associated with the preparation of the samples for the synthesis and analysis were carried out and single crystals were picked up in a dry chamber under nitrogen. The purities of the samples prepared by reaction (1) were confirmed by powder X-ray diffraction data (Stoe STADI-P diffractometer, Cu-Kα$_1$ radiation).

Single-crystal X-ray diffraction analysis was carried out on an automated Brucker SMART CCD diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, 293 K). The crystallographic data and principal details of the structure refinement of $Bi_{10}Nb_3Cl_{18}$ are given in Table 1. The absorption correction was applied using the SADABS program.[11]

Of the two possible space groups, *viz.*, $P6_3$ and $P6_3/m$, the structure was finally solved in the space group $P6_3$ (No. 173),

**Table 1.** Crystallographic data and details of X-ray diffraction study

Parameter	Characteristic
Formula	$Bi_{10}Nb_3Cl_{18}$
Molecular weight	3006.63
Crystal system	Hexagonal
Space group	$P6_3$ (№ 173)
Unit cell parameters	
a/Å	13.787(1)
c/Å	10.650(1)
V/Å^3	1753.2(2)
Z	2
d_{calc}/g cm^{-3}	5.696
μ/cm^{-1}	522.9
Scan mode	ω
Scan range, 2θ/deg	3.5—50
Number of measured reflections	10468
R_{int}	0.146
Number of independent reflections	2052
Number of reflections with $I > 2\sigma(I)$	1753
Number of parameters in refinement	99
$R_1(I > 2\sigma(I))$	0.078
$wR^2(I > 2\sigma(I))/wR^2$ based on all reflections	0.151/0.192
GOOF	1.045

Fig. 1. Fragment of the crystal structure of $Bi_{10}Nb_3Cl_{18}$ (projection onto the ab plane).

because the intensity statistics was indicative of the non-centrosymmetric space group. The coordinates of the bismuth and niobium atoms as well as of some of chlorine atoms were determined by direct methods and refined isotropically and then anisotropically by the full-matrix least-squares method based on F^2. The coordinates of the remaining chlorine atoms were revealed from a series of difference Fourier syntheses alternated with cycles of the least-squares refinement first with isotropic and then anisotropic thermal parameters. The additional Bi^+ cations were found to be disordered over two crystallographic positions with equal occupancies (50%). It should be noted that a satisfactory model for the description of this structure can be obtained in the centrosymmetric space group $P6_3/m$ (No. 176) as well. However, the thermal parameters of the bismuth and chlorine atoms in the latter space group are substantially higher. Moreover, by contrast to the space group $P6_3$ in which the Bi^+ cations are disordered over two positions, these positions in the centrosymmetric space group are averaged, which led to their inadequate description. Therefore, although there are no radical differences between the centrosymmetric and noncentrosymmetric models, the space group $P6_3$ provides a more adequate description of the structure. All calculations were carried our using the SHELX-97 program package.[12]

Magnetic measurements. Magnetic susceptibilities of polycrystalline samples were measured after zero-field cooling on a Quantum Design MPMS2 SQUID magnetometer in the temperature range of 4.2—70 K in the external magnetic field of 5 and 10 Oe.

Results and Discussion

Crystal structure of $Bi_{10}Nb_3Cl_{18}$. X-ray diffraction study demonstrated that the structure of $Bi_{10}Nb_3Cl_{18}$
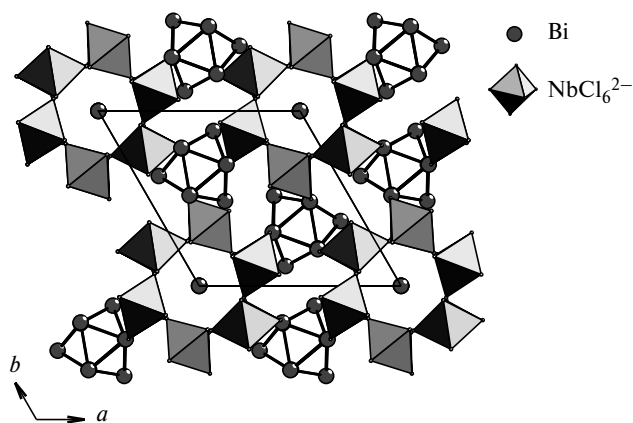
(Fig. 1) is analogous to those of the $Bi_{10}M_3X_{18}$ phases (M = Zr or Hf; X = Cl or Br). The crystal structure of the $Bi_{10}Nb_3Cl_{18}$ compound consists of the Bi_9^{5+} polycations and the octahedral $NbCl_6^{2-}$ anions as the main elements. Besides, the structure contains additional Bi^+ cations. The selected interatomic distances in the structure of $Bi_{10}Nb_3Cl_{18}$ are given in Table 2.

The geometry of the Bi_9^{5+} polycation (Fig. 2) is approximately described by the symmetry group D_{3h} (tricapped trigonal prism). The Bi_9^{5+} polycation has the same symmetry in other phases of the $Bi_{10}M_3X_{18}$ type, unlike the above-mentioned binary compounds Bi_6X_7 (X = Cl or Br) in which the polycation is much more distorted. The structures of all other $Bi_{10}M_3X_{18}$ phases were solved in the centrosymmetric space group with the result that the bismuth positions, which correspond to the Bi(1) and Bi(3) positions in the structure of $Bi_{10}Nb_3Cl_{18}$, became equivalent in these phases. Because of this, the Bi(1)—Bi(1) and Bi(3)—Bi(3) distances, which have different values in the structure under consideration, are averaged in the structures of all other phases. Due to the absence of the center of symmetry in the structure of the $Bi_{10}Nb_3Cl_{18}$ phase, the distances between the atoms belonging to two bases of the tricapped trigonal prism are somewhat different (by ~0.08 Å). For comparison: the distances between the bismuth atoms belonging to the

Table 2. Selected interatomic distances in the structure of $Bi_{10}Nb_3Cl_{18}$

Bond	d/Å	Bond	d/Å
Bi(1)—Bi(1)	3.209(4)	Nb(3)—Cl(1)	2.399(8)
Bi(1)—Bi(2)	3.113(3)	Nb(3)—Cl(2)	2.38(1)
	3.152(3)	Nb(3)—Cl(3)	2.59(1)
Bi(2)—Bi(3)	3.062(3)	Nb(3)—Cl(4)	2.39(1)
	3.075(4)	Nb(3)—Cl(5)	2.43(1)
Bi(3)—Bi(3)	3.291(5)	Nb(3)—Cl(6)	2.32(1)
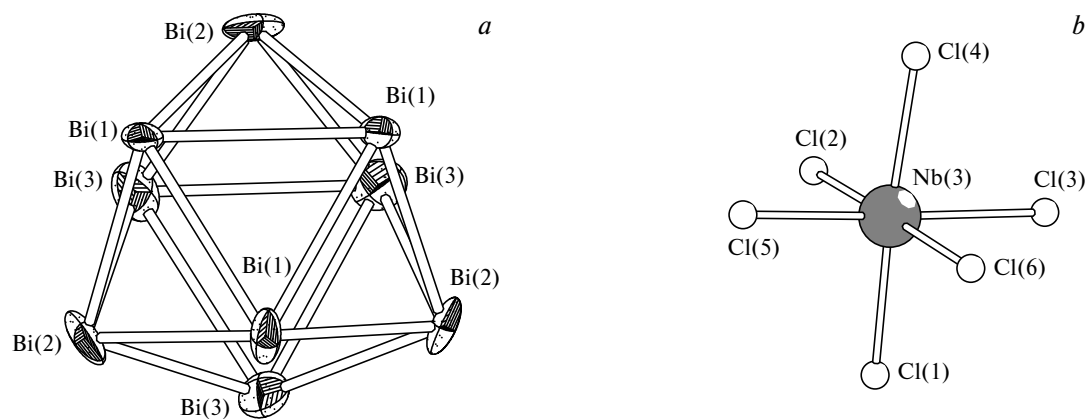
Fig. 2. Main structural units of $Bi_{10}Nb_3Cl_{18}$: *a*, Bi_9^{5+}; *b*, $NbCl_6^{2-}$.

triangular bases of the prism (in $Bi_{10}Nb_3Cl_{18}$, these are Bi(1)—Bi(1) and Bi(3)—Bi(3)), are 3.235 Å in $Bi_{10}Zr_3Cl_{18}$,[8] 3.241 Å in $Bi_{10}Hf_3Cl_{18}$,[5] 3.223 Å in $Bi_9In_{3.67}Cl_{16}$,[8] and 3.249 Å in $Bi_{10}Zr_3Br_{18}$.[7] In the crystal lattice of $Bi_{10}Nb_3Cl_{18}$, the Bi(1)—Bi(1) and Bi(3)—Bi(3) distances give 3.250 Å as the average distance between the atoms forming the base of the prism, which is in good agreement with the above data for the other phases. Therefore, the polycations in all phases of the type under consideration, including the new compound, are very similar in overall geometry and interatomic distances.

Like all other $Bi_{10}M_3X_{18}$-type phases, the $Bi_{10}Nb_3Cl_{18}$ compound contains the octahedral MX_6^{2-} anions, *viz.*, the $NbCl_6^{2-}$ anions, as the counterions (see Fig. 2). As can be seen from Table 2, these octahedra are distorted. Four Nb—Cl distances are virtually equal and are in the range of 2.38—2.43 Å, whereas the Nb(3)—Cl(6) distance is somewhat shorter, and the Nb(3)—Cl(3) distance is substantially elongated. A similar tendency was observed in all other $Bi_{10}M_3X_{18}$-type phases. The MCl_6^{2-} octahedra (M = Zr or Hf) characterized by the average M—Cl distance of 2.44 Å have a shortened bond (2.40 Å) and an elongated bond (2.51—2.53 Å).[5,8] In the $ZrBr_6^{2-}$ octahedra, the distances vary from 2.53 to 2.70 Å.[7] In all cases, the shortest distance occurs between the metal atom and the halogen atom, which is located most closely to the additional Bi^+ cation. Apparently, distortions of the octahedra are associated with the necessity of providing coordination of these ions.

Going to the description of the additional Bi^+ cations, let us note that their interpretation in the crystal structures of these phases presents most difficulties. According to the classical description proposed by Corbett and Friedman[5] for the $Bi_{10}Hf_3Cl_{18}$ compound, the Bi^+ cations form columns along the *c* axis of the unit cell and are disordered, because they occupy an independent fourfold position with an occupancy of 50%. This position cannot be occupied completely because the shortest distance between the atoms in this position related by the symmetry

elements is smaller than 2.5 Å (for the same reason, the Bi atoms cannot be distributed with equal probabilities within this fourfold position). In more recent studies of structural analogs of this phase, no radically different interpretations were proposed for the distribution of the Bi^+ cations. The most serious disagreement with Corbett's model was observed for the structure of $Bi_{10}Zr_3Cl_{18}$ in which the Bi^+ cations are disordered over three positions with different occupancies.[8] X-ray diffraction study of the $Bi_{10}Zr_3Br_{18}$ compound was carried out at low temperature (150 K). However, this study did not provide the answer to the question about the distribution of Bi^+ cations, and the description model remained analogous to that proposed by Corbett.

The X-ray diffraction data for the structure of $Bi_{10}Nb_3Cl_{18}$ did not allow us to give a description of the distribution of Bi^+ cations different from Corbett' model (Fig. 3). Neither attempts to increase the unit cell along the *c* axis nor efforts to solve the structure within lower crystal systems (down to triclinic) led to elimination of disorder of the Bi^+ positions. The only substantial difference from the structure of $Bi_{10}Hf_3Cl_{18}$ is that the choice of the noncentrosymmetric space group enables one to clearly observe the difference between the Bi(4) and Bi(5) positions (see Fig. 3), which would be averaged in the centrosymmetric space group. It can be seen that both bismuth atoms are characterized by anisotropy of thermal vibrations along the *c* axis. However, the anisotropy for Bi(4) is twice as high as that for Bi(5). Evidently, the bismuth atom in the Bi(4) position is less strictly localized than that in the Bi(5) position. However, the X-ray diffraction data did not allow us to elucidate whether this mobility of the cation is true (*i.e.*, within one unit cell) or this is a result of averaging of the cation positions shifted with respect to each other in different unit cells. It should also be noted that there is a relationship between the distribution of the Bi^+ cations in the structure under study and in the $Bi_{10}Zr_3Cl_{18}$ structure (Bi^+ is disordered over three positions). The latter structure can be considered as

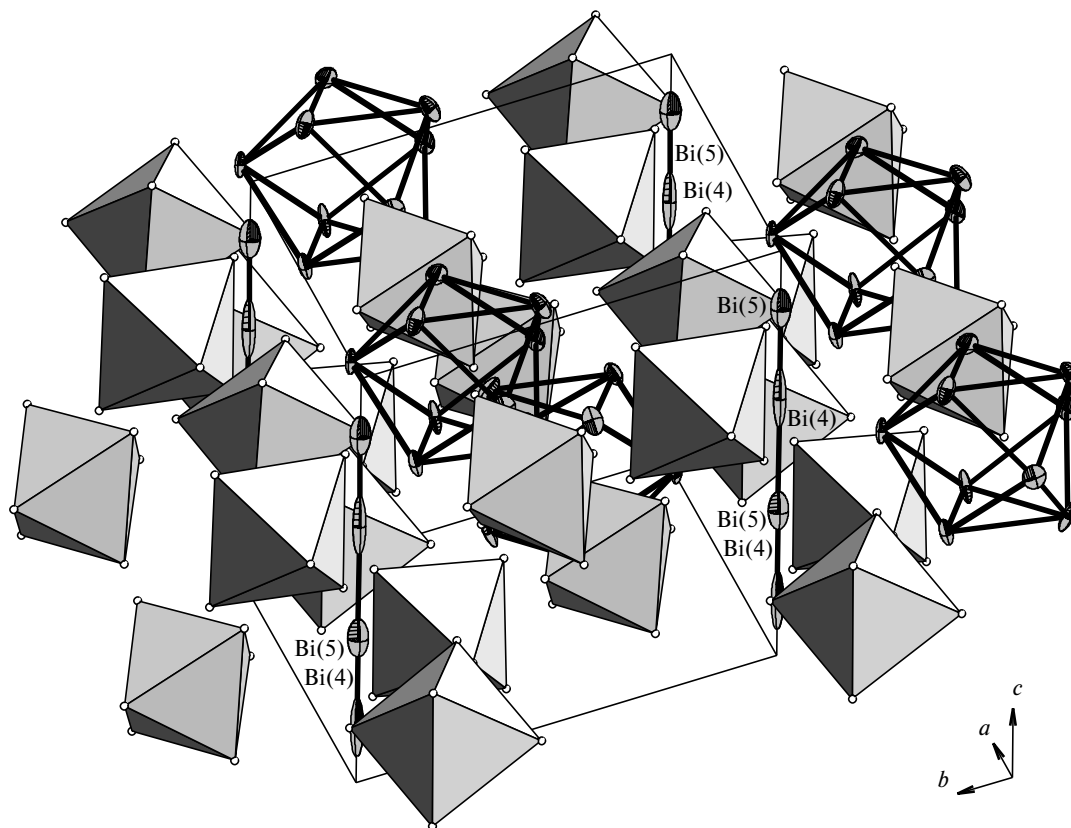**Fig. 3.** View of the columns of the Bi^+ cations (Bi(4) and Bi(5) positions) in the structure of $Bi_{10}Nb_3Cl_{18}$.

the limiting case upon a further increase in anisotropy of the thermal parameter for one of the positions occupied by Bi^+ resulting in its splitting.

The formula of the octahedral $NbCl_6^{2-}$ anions implies that these anions contain Nb^{IV}. Unlike Zr and Hf, for which the formal oxidation state is +4 and, correspondingly, the MCl_6^{2-} anions are most stable, the isolated octahedral $NbCl_6^{2-}$ anions, to our knowledge, were not found in the crystal structures of inorganic compounds. By contrast, the $NbCl_6^-$ anions containing Nb^V as the central ion are typical of Nb (for example, in $KNbCl_6$ [13] or $(TeCl_3)(NbCl_6)$).[14] Since the charges of the ions are not determined independently in the course of structure solution, they are assigned from chemical considerations and taking into account the condition of electroneutrality of the unit cell. Therefore, the hypothesis of the presence of Nb^{IV} requires additional verification. The paramagnetism of the $Bi_{10}Nb_3Cl_{18}$ compound observed in the present study is evidence supporting this hypothesis.

Magnetic properties of $Bi_{10}Nb_3Cl_{18}$. As follows from the temperature dependence of the magnetic susceptibility shown in Fig. 4, the $Bi_{10}Nb_3Cl_{18}$ compound is paramagnetic (inflection of the region of curve *1* at 5—10 K is attributed to the influence of the vessel). Taking into account that Bi_9^{5+} and Bi^+ have no unpaired electrons (this is confirmed by diamagnetism of the $Bi_{10}Hf_3Cl_{18}$ com-

pound[5]), the paramagnetism of the new compound can be associated only with the presence of the paramagnetic central ion in the $NbCl_6^{2-}$ complex anions, *i.e.*, with the presence of Nb^{IV}. Paramagnetism of $Bi_{10}Nb_3Cl_{18}$ cannot be attributed to the presence of impurities of the starting compounds in the samples, whose single-phase state was
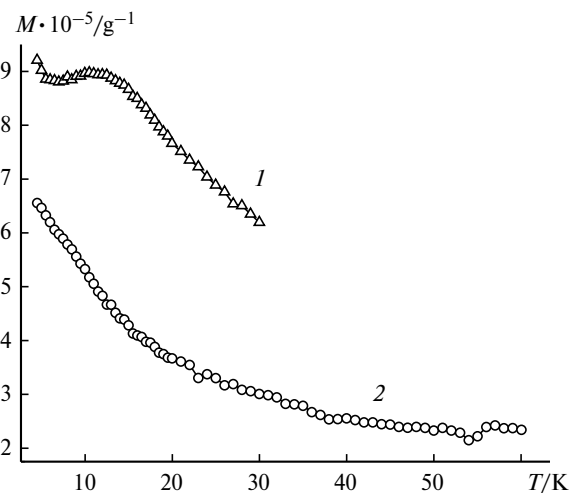

Fig. 4. Temperature dependence of the magnetic susceptibility of $Bi_{10}Nb_3Cl_{18}$ in the external magnetic field of 10 (*1*) and 5 Oe (*2*).

confirmed by powder X-ray diffraction analysis, because possible impurities (small amounts of Bi metal, $BiCl_3$, and $NbCl_5$) are diamagnetic.

Therefore, the Bi_9^{5+} polycations in the $Bi_{10}Nb_3Cl_{18}$ compound coexist with the $NbCl_6^{2-}$ counterions. It is commonly accepted that the anions derived from metal halides in polycation-containing phases are the most stable structural fragments and exert a stabilizing effect. However, the reverse situation is observed in the case of $Bi_{10}Nb_3Cl_{18}$ in which the unstable $NbCl_6^{2-}$ anion is stabilized in the presence of the Bi_9^{5+} polycations. Apparently, taking into account the number of other compounds belonging to the $Bi_{10}M_3X_{18}$ type, this structural motif provides particular stability of phases in the crystalline state, *i.e.*, mutual stabilization takes place.

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