Ab Initio Estimation of NbF_6^-, $NbClF_6^{2-}$, and NbF_7^{2-} Complexes Stability in Alkali Chloride Melts

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Quantum-chemical calculations of the parameters of the $nM^+ \cdot NbClF_6^{2-}$ type particles have been performed, where M stands for Na, K, Cs and $n = 0 - 6$. Under certain conditions such particles may exist in melts of alkali metal chlorides. Within the framework of this approximation, compositions for the most stable particles in molten salts were obtained. Relative stability of the particles containing the NbF_6^-, $NbClF_6^{2-}$, and NbF_7^{2-} complexes has been calculated. Energies and some other characteristics of the electron structure and the particle geometry structure were determined depending on the n and M values. For estimation of the third sphere's influence, the systems $(M_2NbF_7 + 8MCl)$ and $(M_2NbF_7 + 15MCl)$ are surveyed. The chlorine anion enters the first coordination sphere in the Na-system only, i. e. in this system the true complex $NbClF_7^{3-}$ is formed.

Key words: Ab Initio Calculations; Chloride-Fluoride Niobium Complex; Outersphere Cations; Structure Parameters.

1. Introduction

The final goal of our study is the quantum-chemical modelling of charge transfer processes for the redox pair Nb(V)/Nb(IV) in alkali metal chlorides melts containing fluoride niobium complexes NbF_7^{2-} or NbF_6^- of concentrations less than 1 mol %. Theoretical investigations of such level are already available for molten salts [1 – 5].

The main part of our work is the estimation of the particle composition, which exists in bulk melts. As assumed in a previous electrochemical research [6], in the processes of electron transfer, two electroactive particles (and not only one) take part – the original NbF_7^{2-} complex and, presumably, the $NbClF_6^{2-}$ complex.

Based on spectroscopic data and results of physico-chemical analysis, the niobium fluoride complexes in $(M_2NbF_7 + MF)$ melts (M stand for alkali metal) exist in the form of NbF_7^{2-} complexes [7 – 11]. For melts of alkali metal chlorides there are some physico-chemical data only for fluoride complexes of tantalum, crystal-chemical analog of niobium [12, 13]. In these works the results of measurements of viscosity, density, and surface tension in $(K_2TaF_7 + MCl)$ melts are given. The authors assume the existence of the $TaClF_7^{3-}$ complexes in melts at $K_2TaF_7 : MCl \approx 1 : 1$.

Quantum-chemical calculations of electronic structure are found in the literature only for isolated NbF_6^- and TaF_6^- complexes with octahedral structure [14 – 17].

Preliminary results of our quantum-chemical calculations showed that in the absence of outer sphere encirclement stable $NbClF_6^{2-}$ and $NbClF_7^{3-}$ complexes were not formed. In this connection, higher level calculations were performed – namely, the influence of the second coordination sphere (CS) of the complex was taken into account. The particles compositions are $nM^+ \cdot NbClF_6^{2-}$ and $nM^+ \cdot NbClF_7^{3-}$, where n is the number of alkali metal M cations in the outer sphere (OS) shell of $NbClF_6^{2-}$ complexes. These calculations frequently produce a more realistic description of the particles [18 – 23]. According to calculations, the particles containing $NbClF_6^{2-}$ complex are stable in a certain interval of outer sphere compositions. As to the particles containing $NbClF_7^{3-}$ complexes, at the given level of approximation, none of them are formed yet. However, there is a possibility

	$nM^+ \cdot NbF_6^- + Cl^- =$ $nM^+ \cdot NbClF_6^{2-}$ (2)			$(n-1)M^+ \cdot NbF_6^- + MCl =$ $nM^+ \cdot NbClF_6^{2-}$ (3)		
n	Na	K	Cs	Na	K	Cs
1	−300	−267	−227	−268	−219	−179
2	−703	−589	−488	−265	−241	−208
3	−980	−845	−707	−275	−213	−173
4	−1296	−1091	−955	−325	−279	−198
5	−1523	−1308	−1124	−320	−270	−246
	$nM^+ \cdot NbF_7^{2-} + Cl^- =$ $nM^+ \cdot NbClF_6^{2-} + F^-$ (4)			$nM^+ \cdot NbF_7^{2-} + MCl =$ $nM^+ \cdot NbClF_6^{2-} + MF$ (5)		
1	362	303	270	23	56	82
2	439	390	366	100	143	178
3	610	545	468	271	298	280
4	635	585	532	296	337	343
5	634	592	540	295	345	351

Table 1. Energies ΔU (kJ/mol), characterizing mutual stability of the $nM^+ \cdot NbF_6^{1-}$, $nM^+ \cdot NbClF_6^{2-}$, and $nM^+ \cdot NbF_7^{2-}$ particles.

that in some cases, taking into consideration the third CS of the complex, a stabilization can occur for particles of the type $nM^+ \cdot NbClF_7^{2-}$. To verify this assumption, relevant calculations were carried out and some results are given in the following.

2. Computational Details

In this work, results of calculations are presented for the above-mentioned particles $nM^+ \cdot NbClF_6^{2-}$, where M is Na, K, Cs and $n = 1-6$. Geometry optimization and calculations of the particles energies were carried out with the quantum-chemical software PC Gamess/Firefly [24] and the ab initio method (HF level) in the Huzinaga's three gaussian minimal basis set MINI with one additional polarization function for alkali metal atoms (parameter ndfunc = 1). This basis set has been successfully employed earlier [20] for fluoride complexes and is quite sufficient for the given level of the model. In a number of cases, data obtained by the authors for $nM^+ \cdot NbF_7^{2-}$ particles [25] were used in the same basis set.

Structural data relate to particles with the optimized geometric structures. In all cases, search of the optimized geometry was accompanied by control calculation of IR spectra. Thus, all reported data correspond to the true minima on a potential energy surface (imaginary frequencies are absent in IR spectra).

3. Results and Discussion

First, we present data characterizing the stability of complex particles $nM^+ \cdot NbClF_6^{2-}$ relatively to similar particles whose composition includes NbF_6^- or NbF_7^{2-} complexes. These equilibriums are of interest because niobium is usually introduced into the melt as a com-

plex salt such as $MNbF_6$ or M_2NbF_7. This leads to the appearance of the complex ions NbF_6^- or NbF_7^{2-}.

In Table 1, the values of potential energies ΔU for four model reactions with the formation of $nM^+ \cdot NbClF_6^{2-}$ particles are presented. The first two reactions (2), (3) characterize the stability of these particles relatively to the $nM^+ \cdot NbF_6^-$ complexes. Apparently, true energies lie between the values given in this table. These reactions have large negative ΔU energies. Clearly, in this case the transition to Gibbs energies will not lead to essential changes. Therefore, niobium complexes of the type $nM^+ \cdot NbClF_6^{2-}$ cannot exist in the melts of alkali metal chlorides. One should keep in mind that $nM^+ \cdot NbClF_6^{2-}$ particles do not always contain a true $NbClF_6^{2-}$ complex – this will be discussed in more detail later.

The opposite conclusion can be made concerning the possible displacement of the NbF_7^{2-} complex particles by the $NbClF_6^{2-}$ complex. The mutual stability of the particles containing these complexes is characterized by the second pair of equations (4), (5) in Table 1. In these cases, the ΔU energies have large positive values. Therefore, the chloride anion is not capable of displacing the fluoride ligand from the first coordination sphere of niobium in the NbF_7^{2-} complex.

In Figure 1, the energies of formation of the OS shell (E_{os}) for $nM^+ \cdot NbClF_6^{2-}$ (M = Na, K, Cs) particles are given. The values E_{os} were calculated according to the formula

$$E_{os} = E(nM^+ \cdot NbClF_6^{2-}) - E(NbClF_6^{2-}) - nE(M^+), \quad (1)$$

where the particles compositions are shown in round brackets.

For stable particles, i. e., $nM^+ \cdot NbClF_6^{2-}$, the energies corresponding to the optimized geometrical structures are taken. Because the $NbClF_6^{2-}$ complex does
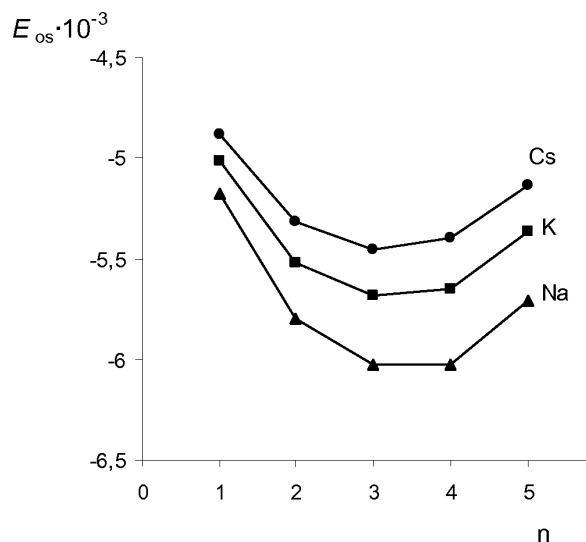
Fig. 1. Energy of the OS shell formation ($E_{os} \cdot 10^{-3}$, kJ/mol) as a function of the number of OS cations (n) for the particles $nM^+ \cdot NbClF_6^{2-}$.

Fig. 2. Dependence of the length of the Nb-Cl (R, Å) bonds upon the number of OS cations (n) for $nM^+ \cdot NbClF_6^{2-}$ particles.

not exist in the free state (in our calculations), the value of the energy corresponding to the geometry in the $2Na^+ \cdot NbClF_6^{2-}$ particle is used. This means that all E_{os} energies are shifted relatively to the non-existent 'true' values by a constant. This shift does not affect the obtained conclusions in any way because we are interested only in relative values of the energies in M and n series.

From Figure 1 it can be seen that particles have the maximum stability at $n = 3$ and 4. The limiting number of the OS cations by the $NbClF_6^{2-}$ complex is equal to five (more exactly, at $n = 6$ the chloride anion leaves the first CS.)

It is not clear to which degree the data shown in Figure 1 are applicable to melts. On the one hand, in the halide melts of alkali metals the average coordination number for the second CS should be more than five. From this point of view, groups with the number of OS cations corresponding to the maximum stability ($n = 3, 4$), cannot exist in noticeable quantities in the bulk of the melt.

On the other hand, a melt is a dynamic structure which allows the realization of various instantaneous configurations including maximally stable ones. Their energy is much lower than for particles with different compositions. For example, the difference in the energy of complexes with $n = 3$ and $n = 5$ is about 300 kJ/mol, and it can be assumed that the life
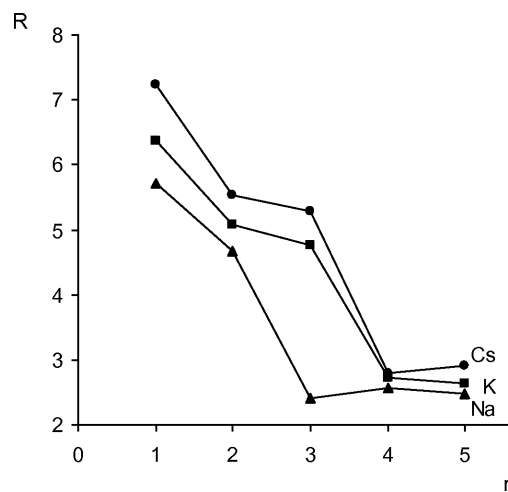
time of the particles with maximum stability will be relatively large.

Leaving the solution of this problem to the future, it should be noted that at the current level of approximation, the difference in the E_{os} energy of complexes with different OS composition is probably overestimated, also it is not clear to which degree. Clearly, calculations taking into account third (or even fourth) CS should be carried out.

In Figure 2 the dependence of the length of Nb-Cl bond upon the composition of the OS shell for complex particles $nM^+ \cdot NbClF_6^{2-}$ is reported. Figure 3 shows examples of the optimized structures containing the chloride anion in the third, second, and first CS of the $NbClF_6^{2-}$ complexes.

Based on these results the following conclusions can be made:

(i) The Cl^- anion can be localize in the 3rd, 2nd or 1st coordination spheres of complex particles depending on the composition of the OS shell.

(ii) The transition of Cl^- to the first CS (which corresponds to the formation of 'true' $NbClF_6^{2-}$ complex) is observed when $n \geq 3$ for Na and $n \geq 4$ for K, Cs.

(iii) For equal n, the length of the R(Nb-Cl) bond decreases in the series Cs > K > Na, with the difference being particularly large for $n = 1-3$ and noticeably smaller for other n. This has a rather simple explanation: for $n < 3$ for all M the chloride anion 'hides' itself behind OS cation in the third or second coordination sphere, i.e., in this case the main contribution in
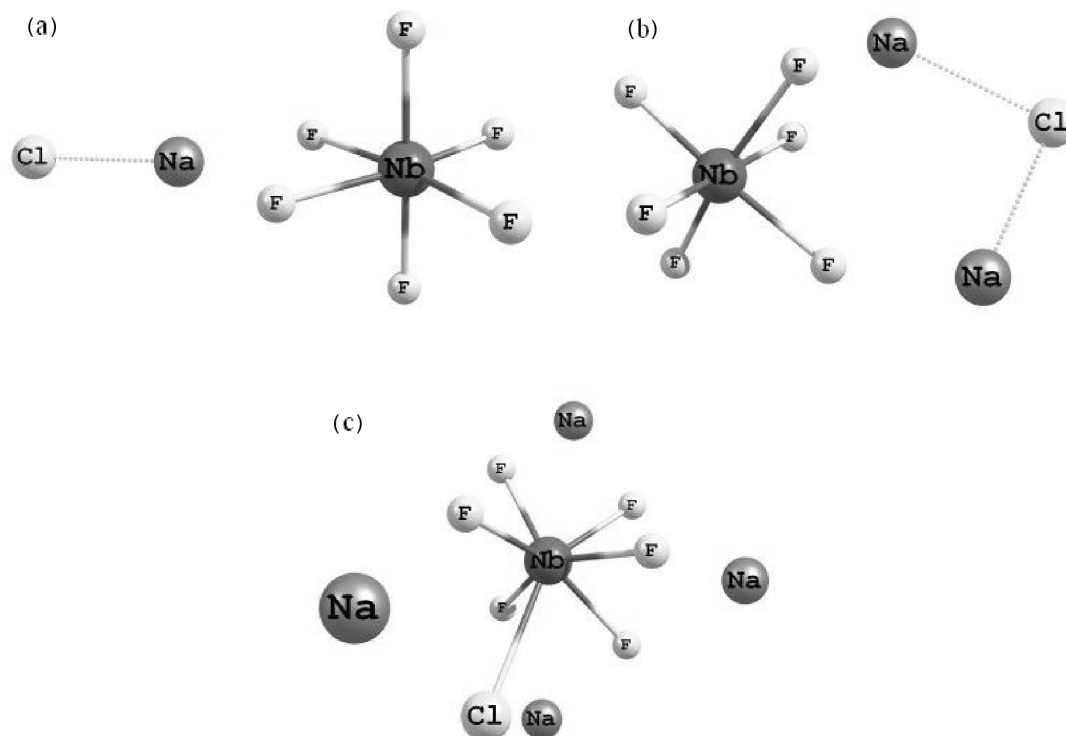
Fig. 3. Geometrical structure of the $Na^+ \cdot NbClF_6^{2-}$ (a), $2Na^+ \cdot NbClF_6^{2-}$ (b), and $4Na^+ \cdot NbClF_6^{2-}$ (c) particles.

Table 2. Average length of (Nb-F) bond for $nM^+ \cdot NbClF_6^{2-}$ particles (in Å).

M	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
Na	1.871	1.882	1.952	1.926	1.938
K	1.869	1.873	1.871	1.908	1.914
Cs	1.867	1.868	1.867	1.899	1.896

Table 3. Charges on the atoms Q (a. u.) for $nM^+ \cdot NbClF_6^{2-}$ particles.

M	n	Q = Nb	Q = F	Q = Cl	Q = M
–	0	1.228	−0.379	−0.981	–
Na	1	1.371	−0.350	−0.574	0.306
	2	1.476	−0.318	−0.421	0.427
	3	1.325	−0.325	−0.206	0.610
	4	1.397	−0.318	−0.214	0.681
	5	1.391	−0.307	−0.156	0.721
K	1	1.318	−0.359	−0.692	0.530
	2	1.375	−0.348	−0.579	0.645
	3	1.391	−0.343	−0.561	0.742
	4	1.290	−0.357	−0.377	0.807
	5	1.271	−0.350	−0.341	0.834
Cs	1	1.277	−0.368	−0.790	0.720
	2	1.308	−0.364	−0.710	0.791
	3	1.318	−0.360	−0.704	0.848
	4	1.195	−0.377	−0.490	0.890
	5	1.231	−0.371	−0.500	0.899

the difference of the R(Nb-Cl) values for different M comes from the significant difference of OS cations size. The transition of the chloride anion into the first CS noticeably decreases this difference.

It is also worth pointing out some regularities of the average lengths of Nb-F bonds (see Table 2).

(iv) For a given n, these values decrease in the series Na > K > Cs. This series is the opposite to the series in which the length of Nb-Cl bond decreases (see above). The dependence of R(Nb-F) upon the type of OS cation corresponds to the simple concept of the competition over the fluoride between niobium and the cations of the second coordination sphere.

(v) Comparing the data from Table 2 and Figure 2, one can make a conclusion that when chloride enters the first CS, the length of the Nb-F bond makes a leap

(by 0.07 Å for Na-, 0.037 for K-, and 0.032 for Cs-particles).

Table 3 reports the values of atom charges by Lovdin (definition see in [26]) for $nM^+ \cdot NbClF_6^{2-}$ particles. For individual $NbClF_6^{2-}$ complex ($n = 0$) the geomet-

ric structure of $NbClF_6^{2-}$ from $2Na^+ \cdot NbClF_6^{2-}$ particle was used as before. For fluoride atoms and OS cations, average charges are shown.

The comparison of the charges on atoms of the particles under study demonstrates that the chloride atom reveals the highest donor ability when charges on atoms are redistributed in the process of increasing the number of OS cations. With the increase of n the charges on the fluoride and niobium atoms change only slightly whereas for chloride and OS cations significant decrease of the charges (in absolute values) is observed in this series.

For equal values of n, the negative charge of the chloride anion decreases (in absolute value) in the series of OS cations as follows: $Q(Cl)^{Cs} > Q(Cl)^K > Q(Cl)^{Na}$. Correspondingly, the charge of the OS cations changes as follows: $Q(Cs) > Q(K) > Q(Na)$. Therefore, the transfer of the electron density occurs mainly to the OS cations and is determined by the polarizing capability of the cation.

It should be noted, however, that at some values of n, the niobium cation is also a donor in relation to the OS cations, although weaker than chloride.

In Figure 4 'differential' curves of the changes in the charge on the chloride atom (ΔQ) for $nM^+ \cdot NbClF_6^{2-}$ particles are shown depending on the type and number of OS cations. The ΔQ values were calculated according to the expression $\Delta Q = Q_n - Q_{(n-1)}$.

Comparing Figure 2 and Figure 4, it can be seen that the maximum change of the charge ΔQ is observed for those values of n that correspond to the entry of the chloride ligand into the first coordination sphere of the
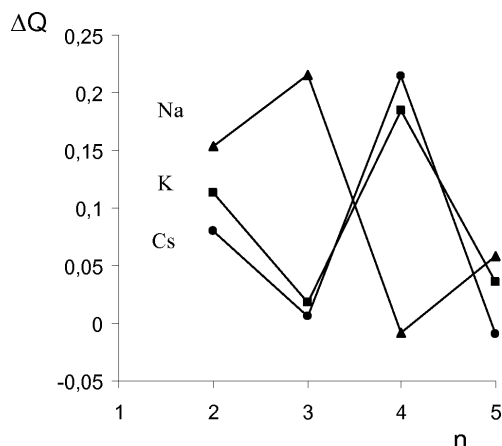
Table 4. Values of bond orders B_{ij} for $nM^+ \cdot NbClF_6^{2-}$ particles.

M	n	B_{ij}	
		Nb – F	M – Cl
Na	1	0.705	0.547
	2	0.748	0.355
	3	0.595	0.110
	4	0.769	0.098
	5	0.726	0.082
K	1	0.805	0.447
	2	0.895	0.491
	3	0.865	0.304
	4	0.806	0.106
	5	0.797	0.085
Cs	1	0.826	0.321
	2	0.887	0.344
	3	0.864	0.225
	4	0.818	0.088
	5	0.824	0.081

complex particle.

In Table 4 calculated values of the average values of the bond orders [27] Nb-F and M-Cl (B_{ij}) are presented.

Comparing the data presented in this table and in Figure 2, one can see that the values of bond orders B_{ij}(M-Cl) make sudden changes at the transition of the chloride anion from one CS to another. As chloride anion approaches the central ion of the complex, the bonds between Cl^- and OS cations weaken.

At the same time, the values of B_{ij} for Nb-F bonds change much weaker in the n series. The dependence of B_{ij}(Nb-F) upon the type of OS cation corresponds to the character of the length change of the Nb-F bonds (see above), namely, the covalent component of the Nb-F bond decreases in the $Cs > K > Na$ series, causing antibatic change of the R(Nb-F) bond length.

Thus, such parameters of the complex electronic structure as bond orders and atom charges change in accordance with the changes in the geometric srtucture of the complexes.

There is, however, one problem, namely, the influence of a long-range environment on the structure of niobium complexes. Here various approaches are possible: the account of the long-range interaction using polarizabilities obtained in the spirit of works [28–32], the adjustment of suitable models built in quantum-chemical programs, etc. However, now the problem has no conventional solution for alkali metals halide melts. In this connection, we have made a simple estimation of the influence of the

Fig. 4. Change of the charge ΔQ (a. u.) on the chloride atom for $nM^+ \cdot NbClF_6^{2-}$ particles.

Table 5. Average values of the (Nb-F) distances r(Nb-F) and minimal Nb-Cl distances r(Nb-Cl)$_{min}$ for the ($M_2NbF_7 + 8MCl$) (**I**) and ($M_2NbF_7 + 15MCl$) (**II**) systems.

	Na		K		Cs	
	(I)	(II)	(I)	(II)	(I)	(II)
r(Nb-F)	1.985	1.982	1.933	1.936	1.933	1.934
r(Nb-Cl)$_{min}$	2.605	2.616	4.048	4.259	4.459	5.093

long-range environment, based on the results of [33]. In this work, it is shown that charged clusters are not suitable to model the first CS of gadolinium chloride complexes in MCl melts. The use of neutral clusters is preferable. In the given work, calculations for systems ($M_2NbF_7 + 8MCl$) (**I**) and ($M_2NbF_7 + 15MCl$) (**II**) are made. Eight molecules MCl are not enough for the complete filling of the third CS of niobium complexes, but the results obtained for system (**I**) are useful from a methodological point of view.

The following results are obtained (see Table 5).

i) In the Na-Systems (**I**) and (**II**) the chlorine anion enters the first CS, i. e. the true $NbClF_7^{3-}$ complex is formed. Thus, in this case, increasing the number of atoms in the system has essentially affected result.

The r(Nb-Cl)$_{min}$ values of minimal (Nb-Cl) distance in these cases are longer than in the complexes $nM^+ \cdot NbClF_6^{2-}$ at $n = 3-5$ (where Cl^- anion is also located in the first CS). These values are equal to 2.61 Å and 2.62 Å in Table 5 in comparison with $2.42-2.57$ Å in Figure 2. This is not surprising because in Systems (**I**) and (**II**) the first coordination number of the niobium complex is 8 while in the $nM^+ \cdot NbClF_6^{2-}$ systems it is 7.

ii) In the K- and Cs-Systems (**I**) and (**II**) chlorine anions are located out of the first CS of the Nb complex. The r(Nb-Cl)$_{min}$ values correspond to the second CS. In these systems, the average values of the (Nb-F) bond length are less than in $3M^+ \cdot NbClF_6^{2-}$ and $3M^+ \cdot NbClF_6^{2-}$, where the Cl^- anion is located in the second CS also. However, comparison of these systems is not quite correct as in K- and Cs-Systems of types (**I**) and (**II**) the Nb complex has the composition NbF_7^{2-} instead of $NbClF_6^{2-}$. Complexes $3K^+ \cdot NbF_7^{2-}$ and $3Cs^+ \cdot NbF_7^{2-}$ are more suitable. Here the average values of the (Nb-F) bond length vary in the limits $1.931-1.933$ Å for K^+ and $1.925-1.928$ Å

for Cs^+ [34]. Comparing these values with the data in Table 5, we see that the difference is insignificant. Probably, the main cause to the weak dependence of these quantities on the composition of a complex environment is the competition for fluorine ligand between the niobium and the alkali metal cations located in the second OS.

For the same reason, the (Nb-F) bonds in $3M^+ \cdot NbF_7^{2-}$ particles are weakened in comparison with isolated complexes NbF_7^{2-} (for the latter, the average length of the (Nb-F) bond is 1.922 Å).

Conclusions

According to the calculations at this level of approximation, the chloride anions in melts of alkali metals chlorides containing NbF_6^- complexes should enter the first or the second coordination sphere of the complex. In melts containing Na^+ cations, the chloride anion should certainly enter the first CS forming a 'true' $NbClF_6^{2-}$ complex. As for the melts containing K^+ and Cs^+ cations, the situation is less clear and further investigations with more complicated systems are needed. Based on the composition of the OS shell corresponding to the most stable particles with $n = 3$ (see Fig. 1), Cl^- should be localize in the second, not the first, CS of the NbF_6^- complex.

In melts containing NbF_7^{2-} complexes the displacement of fluoride ligands by chloride anions should not take place. This conclusion can be probably considered as trustworthy. However, in all considered systems the influence of the third CS results in additional stabilization of the chlorine anion near to the fluoride complex NbF_7^{2-}. In the Na-system, the true $NbClF_7^{3-}$ complex is formed. In K- and Cs-systems, at least one Cl^- anion is located in the second, but not in the third, CS.

The transition from charged particles such as $nM^+ \cdot NbF_7^{2-}$ to the neutral clusters (**I**) and (**II**) does not lead to essential change of (Nb-F) bond lengths.

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