Ab Initio Estimation of NbF$_6^-$, NbClF$_2^-$, and NbF$_7^{2-}$ Complexes Stability in Alkali Chloride Melts

Vyacheslav G. Kremenetsky$^a$, Sergey A. Kuznetsov$^a$, Olga V. Kremenetskaya$^b$, Veniamin V. Soloviev$^c$, Lyudmila A. Chernenko$^c$, and Anatoliy D. Fofanov$^b$

$^a$ Institute of Chemistry, Kola Science Center RAS, 26a Akademgorodok, 184209 Apatity, Russia
$^b$ Petrozavodsk State University, Lenin avenue 33, 185910 Petrozavodsk, Russia
$^c$ Poltava National Technical University, Pershotravnevyi prospekt 24, 36011 Poltava Ukraine

Reprint requests to Dr. V. G. K.; E-mail: kreme

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Quantum-chemical calculations of the parameters of the $nM^+\cdot$NbClF$_2^-$ 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$_2^-$, 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$_3^-$ 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$_2^{2-}$ 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$_2^-$ complex.

Based on spectroscopic data and results of physico-chemical analysis, the niobium fluoride complexes in (M$_2$NbF$_7$ + MF) melts (M stand for alkali metal) exist in the form of NbF$_2^{2-}$ complexes [7 – 11]. For melts of alkali metal chlorides there are some physico-chemical data only for fluoride complexes of tantalum, crystalchemical analog of niobium [12, 13]. In these works the results of measurements of viscosity, density, and surface tension in (K$_2$TaF$_7$ + MCl) melts are given. The authors assume the existence of the TaClF$_3^-$ complexes in melts at K$_2$TaF$_7$: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$_2^-$ and NbClF$_3^-$ 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 particle compositions are $nM^+\cdot$NbClF$_2^-$ and $nM^+\cdot$NbClF$_3^-$, where $n$ is the number of alkali metal M cations in the outer sphere (OS) shell of NbClF$_2^-$ complexes. These calculations frequently produce a more realistic description of the particles [18 – 23]. According to calculations, the particles containing NbClF$_2^-$ complex are stable in a certain interval of outer sphere compositions. As to the particles containing NbClF$_3^-$ complexes, at the given level of approximation, none of them are formed yet. However, there is a possibility...
that in some cases, taking into consideration the third CS of the complex, a stabilization can occur for particles of the type \( nM^+ \cdot NbClF_6^{2-} \). 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 Games/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 \( nM^+ \cdot NbF_2^{2-} \) particles [25] were used in the same basis set.

Structural data relate to particles with the optimized geometrical 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 \( NbF_6^2- \) or \( NbF_7^2- \) complexes. These equilibriums are of interest because niobium is usually introduced into the melt as a complex salt such as \( MNbF_6 \) or \( M_2NbF_7 \). This leads to the appearance of the complex ions \( NbF_6^2- \) or \( NbF_7^2- \).

In Table 1, the values of potential energies \( \Delta U \) 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 \( nM^+ \cdot NbF_6^{2-} \) complexes. Apparently, true energies lie between the values given in this table. These reactions have large negative \( \Delta U \) 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 \( \Delta U \) 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

\[
E_{os} = E(nM^+ \cdot NbClF_6^{2-}) - E(NbClF_6^{2-}) - nE(M^+) ,
\]


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...
not exist in the free state (in our calculations), the value of the energy corresponding to the geometry in the $2\text{Na}^+ \cdot \text{NbClF}_2^-_6$ particle is used. This means that all $E_{\text{os}}$ 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$_2^-_6$ 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 $E_{\text{os}}$ 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 (R, Å) bonds upon the number of OS cations ($n$) for $nM^+ \cdot \text{NbClF}_2^-_6$ particles.

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$_2^-_6$ 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
the difference of the R(Nb-Cl) values for different Mcomes 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⁺ · NbClF⁶⁻ particles. For individual NbClF⁶⁻ complex (n = 0) the geomet-
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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: $Q(Cs)_{Na} > Q(K)_{Na} > Q(Na)$. 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 Table 4 calculated values of the average values of the bond orders $B_{ij}$ 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 structure 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

<table>
<thead>
<tr>
<th>$n$</th>
<th>$Na$</th>
<th>$K$</th>
<th>$Cs$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.705</td>
<td>0.805</td>
<td>0.826</td>
</tr>
<tr>
<td>2</td>
<td>0.748</td>
<td>0.895</td>
<td>0.887</td>
</tr>
<tr>
<td>3</td>
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<td>0.865</td>
<td>0.864</td>
</tr>
<tr>
<td>4</td>
<td>0.769</td>
<td>0.806</td>
<td>0.818</td>
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<tr>
<td>5</td>
<td>0.726</td>
<td>0.797</td>
<td>0.824</td>
</tr>
</tbody>
</table>

In Table 4 calculated values of the average values of the bond orders [27] Nb-F and M-Cl ($B_{ij}$) are presented.
Table 5. Average values of the (Nb-F) distances $r$(Nb-F) and minimal Nb-Cl distances $r$(Nb-Cl)$_{\text{min}}$ for the (M$_2$NbF$_7$ + 8MCl) (I) and (M$_2$NbF$_7$ + 15MCl) (II) systems.

<table>
<thead>
<tr>
<th></th>
<th>Na (I)</th>
<th>K (I)</th>
<th>Cs (I)</th>
<th>Na (II)</th>
<th>K (II)</th>
<th>Cs (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r$(Nb-F)</td>
<td>1.985</td>
<td>1.982</td>
<td>1.933</td>
<td>1.936</td>
<td>1.933</td>
<td>1.934</td>
</tr>
<tr>
<td>$r$(Nb-Cl)$_{\text{min}}$</td>
<td>2.605</td>
<td>2.616</td>
<td>4.048</td>
<td>4.259</td>
<td>4.459</td>
<td>5.093</td>
</tr>
</tbody>
</table>

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$_2$NbF$_7$ + 8MCl) (I) and (M$_2$NbF$_7$ + 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$_5^-$ complex is formed. Thus, in this case, increasing the number of atoms in the system has essentially affected result.

The $r$(Nb-Cl)$_{\text{min}}$ values of minimal (Nb-Cl) distance in these cases are longer than in the complexes nM$^+$.NbClF$_5^-$ 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$^+$.NbClF$_5^-$ 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)$_{\text{min}}$ values correspond to the second CS. In these systems, the average values of the (Nb-F) bond length are less than in 3M$^+$.NbClF$_6^-$ and 3M$^+$.NbClF$_2^-$, 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$_3^-$ instead of NbClF$_2^-$. Complexes 3K$^+$.NbF$_3^-$ and 3Cs$^+$.NbF$_3^-$ 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$^+$. 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$^+$.NbF$_3^-$ particles are weakened in comparison with isolated complexes NbF$_3^-$ (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 chlorine anion should certainly enter the first CS forming a ‘true’ NbClF$_3^-$ 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$_3^-$ 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$_3^-$. In the Na-system, the true NbClF$_2^-$ 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$^+$.NbF$_3^-$ to the neutral clusters (I) and (II) does not lead to essential change of (Nb-F) bond lengths.

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