

The Electronic Structure of Anionic Halide Complexes of Element 105 in Aqueous Solutions and Their Extraction by Aliphatic Amines

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Abstract

To study the complex formation of group 5 elements (Nb, Ta, Ha, and pseudoanalog Pa) in aqueous HCl solutions of medium and high concentrations the electronic structures of anionic complexes of these elements $[MCl_6]^-$, $[MOCl_4]^-$, $[M(OH)_2Cl_4]^-$, and $[MOCl_5]^{2-}$ have been calculated using the relativistic Dirac-Slater Discrete-Variational Method. The charge density distribution analysis has shown that tantalum occupies a specific position in the group and has the highest tendency to form the pure halide complex, $[TaCl_6]^-$. This fact along with a high covalency of this complex explains its good extractability into aliphatic amines. Niobium has equal trends to form pure halide $[NbCl_6]^-$ and oxyhalide $[NbOCl_5]^{2-}$ species at medium and high acid concentrations. Protactinium has a slight preference for the $[PaOCl_5]^{2-}$ form or for the pure halide complexes with coordination number higher than 6 under these conditions. Element 105 at high HCl concentrations will have a preference to form oxyhalide anionic complex $[HaOCl_5]^{2-}$ rather than $[HaCl_6]^-$. For the same sort of anionic oxychloride complexes an estimate has been done of their partition between the organic and aqueous phases in the extraction by aliphatic amines, which shows the following succession of the partition coefficients: $P_{Nb} < P_{Ha} < P_{Pa}$.

1. Introduction

1.1. Experimental study of element 105 in aqueous solutions

The first experimental study [1] of element 105 in aqueous solutions was aimed at proving the classification of it as a *d* element. The following two approaches confirmed this idea. In the first approach hahnium was shown to adhere to glass surfaces upon fuming

with concentrated nitric acid, a property characteristic of group 5 elements, Nb and Ta. In the second approach the extraction of Ha from acidic fluoride solutions into methylisobutylketone (MIBK), the process which is well known and used as a separation and purification for group 5 elements (Nb and Ta), was attempted. These latter experiments revealed that Ha is not extracted under conditions where Ta is quantitatively extracted. One possible explanation was the formation of non-extractable $[HaF_7]^{2-}$ species or other polynegative fluoride complexes in contrast to $[TaF_6]^-$. The other explanation was the possibility of Ha to form Ha^{3+} ions due to a strong relativistic stabilization of the $7s^2$ electrons.

Concerning the latter assumption, multiconfiguration Dirac-Fock atomic calculations (MCDF) [2] have shown that the main electronic configuration for Ha^{3+} is $6d^2$ and the multiple ionization potential $(0)-(3+)$ for Ha is higher than those for Nb and Ta. Estimates of the standard electrode potentials [3] based on the MCDF calculations confirmed no extra stability of the oxidation state +3 for Ha. The given value of the standard potential for the couple Ha^{4+}/Ha^{3+} is -1.38 V and the stability of the trivalent state in aqueous solutions was shown to decrease in the succession $V > Nb > Ta > Ha > Pa$.

The next series of the extraction chromatography experiments [4] studied the halide complexation of element 105 under conditions where Nb, Ta, and Pa are extracted into triisooctyl amine (TIOA). ^{262}Ha was shown to be absorbed on the column from either 12 M HCl/0.02 M HF or 10 M HCl solutions like its homologs Nb and Ta, and like pseudohomolog Pa. Elutions of ^{262}Ha were performed in a) 10 M HCl/0.025 M HF [4], b) 4 M HCl/0.02 M HF [4], and c) 0.5 M HCl/0.01 M HF [5]. The very strong halide complexes of Ta were not eluted from the columns in either of these solutions and had to be stripped with 6 M HNO_3 /0.015 M HF. ^{262}Ha was found to be eluted between Nb and Pa in a), with Nb and Pa in

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b), and close to Pa in c), showing that the anionic halide complexes of Ha are different from those of Ta, and are more like those of Nb and Pa. Thus Ha turned out to behave differently from Ta at nearly all acid molarities.

Results of the extraction experiments [6] on Ha, Nb, and Pa into diisobutylcarbinol (DIBC) from aqueous HBr and HCl solutions indicated that the tendency of element 105 to form polynegative complexes at high halide concentration is stronger than for Nb and much stronger than for Pa.

Summarizing the results of the extraction chromatography experiments, one can say that element 105 is stable in the highest oxidation state +5 and that it forms anionic complexes, a property characteristic of the group 5 elements, but these complexes are similar to those of Nb and Pa and different from those of Ta.

1.2. Anionic forms of group-5 elements in aqueous solutions

The unsimilarity of Ta and Nb towards formation of different halide complexes is well known. The historical method of separation of Nb and Ta is based on the crystallization of K_2TaF_7 and $K_2NbOF_5 \cdot 2H_2O$ from dilute HF solutions. In fact the occurrence of $[NbF_6]^-$, $[NbF_7]^{2-}$ or $[NbOF_5]^{2-}$, $[Nb(OH)_2F_5]^{2-}$ depends on the HF concentration, while Ta forms as a rule $[TaF_6]^-$ or $[TaF_7]^{2-}$ complexes [7]. Relative to fluoride complex formation, protactinium behaves similar to tantalum especially at higher concentration forming $[PaF_6]^-$, $[PaF_7]^{2-}$, or $[PaF_8]^{3-}$.

Analogously, in hydrochloric acid solutions niobium forms $[NbOCl_4]^-$ or $[Nb(OH)_2Cl_4]^-$ at low concentrations and $[NbOCl_5]^{2-}$ at higher molarities while tantalum forms $[TaCl_6]^-$, $[TaCl_7]^{2-}$. At HCl concentrations > 12 M niobium can form as well $[NbCl_6]^-$ species. This difference in the complex formation between Nb and Ta is the basis of their amine separation [8].

The availability of hydrolyzed oxochloro complexes in acid solutions of protactinium at low and medium HCl concentrations is known [9]. At concentrations below 3 M protactinium forms $[PaOOH]^{2+}$, $[PaO(OH)Cl]^+$, $[Pa(OH)Cl_3]^+$, $[Pa(OH)_3Cl]^+$, $[Pa(OH)_2Cl_2]^+$, and some neutral complexes such as $PaOCl_3$, $Pa(OH)_2Cl_3$, and $PaO(OH)Cl_2$. At concentrations between 3 M and 5 M protactinium is present mainly as $[PaO_2Cl_2]^-$, $Pa(OH)Cl_4$, $[PaO(OH)Cl_3]^-$, $[PaOCl_4]^-$ or $[Pa(OH)_2Cl_4]^-$ and at > 6 M HCl complexes such as $[PaOCl_5]^{2-}$, $[Pa(OH)Cl_5]^-$, $[Pa(OH)_2Cl_5]^{2-}$, or $[Pa(OH)Cl_6]^{2-}$ are predominant [10]. At even higher concentrations, formation of the pure halide complexes like $[PaCl_6]^-$, $[PaCl_7]^{2-}$, $[PaCl_8]^{3-}$, and some others starts [11].

In the HF + HCl medium the niobium complex retains oxygen ($[NbOCl_4]^-$, $[NbOCl_5]^{2-}$, $[NbOCl_3F_2]^{2-}$, $[NbOF_5]^{2-}$) unless HF concentration becomes high and part or all of the oxygen can be replaced by the

fluoride ion [12]. Upon the addition of HF tantalum changes to chloride fluoride complexes, such as $[TaCl_5F]^-$, $[TaCl_5F_2]^{2-}$, $[TaF_7]^{2-}$ and others.

Protactinium in HF + HCl solutions forms $[PaF_xCl_y]^{x+y-5}$ or $[PaOF_xCl_y]^{x+y-3}$ complexes, where x and y depend on the $[Cl^-]$ and $[F^-]$ concentrations. Formation of pure fluoride complexes even at low $[F^-]$ concentrations is quite probable [13].

The different extraction behavior of Nb and Pa in comparison with Ta at many HCl concentrations is connected with the complex formation of the extractable halide complexes and their structural differences. The fact that in elution with 4 M HCl/0.02 M HF (Pa–Nb fraction), and with 6 M HNO_3 /0.015 M HF (Ta fraction) hahnium was found in the Nb–Pa phase and not in the Ta one caused the authors of Refs. [4–6] to arrive at the conclusion that the complexes of hahnium might have the same oxyhalide forms, $[HaOCl_4]^-$, $[Ha(OH)_2Cl_4]^-$, or $[HaOCl_5]^{2-}$, as those of Nb and Pa, and not $[HaCl_6]^-$, as that of Ta. The tendency of Ha to form multicharged anionic complexes at high halide concentrations [6] gives possibly an additional proof in favour of forming $[HaOCl_5]^{2-}$ or other multicharged halide complexes, like $[HaCl_7]^{2-}$.

The structural differences of group 5 halide complexes must be connected with the electronic structure of the central metal ion, namely with the different involvement of its valence orbitals in the chemical bonding. In Ref. [4] the following suggestion for the possibly different involvement of the valence orbitals of group 5 elements has been given. The relatively small radial extension of the $4d$ wave functions of Nb favours the formation of relatively short Nb=O bonds. The more expanded $5d$ functions of Ta have a stronger overlap with large ligands, and with their bigger number thus forming $[TaCl_6]^-$ or $[TaCl_7]^{2-}$. In Ha complexes, the situation was supposed to be so that due to relativistic effects the $6d$ orbitals become energetically less accessible and their contribution to bonding is diminished. As a result, Ha again forms relatively short bonds with oxygen and in a way the trend in the group to pure halide complex formation seems to be reversed.

This discussion together with the interesting results of the experiments [4–6] gave impact to the relativistic molecular orbital calculations presented in this paper. The calculations have been done for $[MCl_6]^-$, $[MOCl_4]^-$, $[M(OH)_2Cl_4]^-$, and $[MOCl_5]^{2-}$ ($M = Nb, Ta, Ha, Pa$) complexes with the aim to understand the role of different orbitals in the chemical bond formation and the differences in the halide complexing of the group 5 elements.

In Sec. 2 structural experimental data on oxyhalide and halide complexes of Nb, Ta, and Pa are given. Sec. 3 contains a short description of the relativistic Dirac Slater Discrete Variational Method (DS DV) and some details of the calculations. In Sec. 4 results and their discussion are presented. Sec. 5 is devoted to the consideration of the extraction of the anionic

halide species by aliphatic amines. Conclusions are presented in Sec. 6.

2. Structures of the halide- and oxyhalide complexes of Nb, Ta, and Pa

Most of the crystallographic data [7] are available for the fluoride anhydrous complexes of Nb and Ta. K_2NbF_7 and K_2TaF_7 contain seven-coordinated metal ions, six fluorine atoms being arranged as a distorted trigonal prism with the seventh atom bonded through one of the faces of the distorted prism. The lattice $KNbF_6$ contains discrete $[NbF_6]^-$ ions, a slightly distorted octahedron of six F atoms, with a mean Nb–F bond distance of 2.14 Å. $KTaF_6$ crystallizes with the same arrangement. K_2NbOF_5 contains discrete $[NbOF_5]^{2-}$ ions. This complex ion has a bipyramidal structure with C_{4v} symmetry, the Nb–O bond length being 1.68, Nb–F₁ 2.06, and Nb–4F₂ 1.84 Å. In the hydrazinium salt $[NbOF_4]^-$ ion has a distorted octahedral configuration (Nb=O: 1.75 Å) [14]. The $[NbOF_4]^-$ ion contains Nb–O–Nb bridges.

Raman spectra were taken to indicate O_h symmetry of the $[MCl_6]^-$ ions in $A[MCl_6]$ complexes (M = Nb, Ta; A = Li, Na, K, Rb, Cs, Tl). In $PPh_4[NbCl_6]$ the anion $[NbCl_6]^-$ has C_{4v} symmetry with a mean Nb–Cl distance equal to 2.33 Å. In many other compounds of $[NbCl_6]^-$ the metal displays octahedral coordination with M–Cl distances ranging from 2.29 to 2.37 Å. Compounds of Ta have similar structures and bond lengths.

A structure of Cs_2NbOCl_5 was determined and the Nb–Cl distance was found to be equal to 2.15 ± 0.05 Å [15]. The structure of $[NbOCl_5]^{2-}$ in $(AsPh_4)_2[NbOCl_5]$ shows an octahedral arrangement of oxygen atoms [14] with a very long Nb=O distance of 1.97 Å.

IR spectra for $(R_3NH)[NbOCl_4]$ indicated the presence of –Nb–O–Nb–O–Nb– chains. In $[NbCl_4(diams)_2][NbOCl_4]$, the anion $[NbOCl_4]^-$ is basically a square pyramid with the oxygen at the apex (Nb=O: 1.70 Å) and a mean Nb–Cl distance of 2.37 Å [14].

For aqueous solutions, IR spectroscopy [16] shows that $[NbOCl_4]^-$ contains the chains –Nb–O–Nb–O–Nb–.

Protactinium is known to form solid state halide compounds with high coordination numbers (CN). Thus Pa in solid $RbPaF_6$ has CN = 8. The structure of $(NEt_4)_2PaOCl_5$ has been reported [17]. The $[PaOCl_5]^{2-}$ ion has a distorted octahedral arrangement around the Pa atom with Pa=O: 1.74 Å and Pa–Cl distances varying from 2.42 to 2.72 Å.

In the experiments [14–16] all the species under investigation, however, are monomers since the elements are produced with low production rates in nuclear reactions in a reactor or accelerator.

3. Method and details of the calculations

3.1. Self-Consistent-Charge Dirac-Slater Discrete Variational (SCC DS DV) method

Calculations of the anionic halide and oxyhalide complexes of group 5 elements have been done using the relativistic DS DV method with SCC approximation [18]. The description of the method and its application to gas-phase compounds of the group 5 elements are given elsewhere [18–21].

The symmetry molecular orbitals were constructed for the double point groups.

Calculations have been done within both the full electron and frozen core approximations. The basis set included valence $(n-1)d_{3/2}$, $(n-1)d_{5/2}$, ns , $np_{1/2}$, and $np_{3/2}$ orbitals. Numerical integration was done using 9000 integration points.

The Mulliken population analysis has been used to analyze the electron density distribution: effective atomic charges, atomic orbital populations, and overlap populations (partial and total). The partial overlap populations between orbitals j and k on centers r and s are expressed as follows

$$n(j_r, k_s) = \sum_i n(i; j_r, k_s) = \sum_i 2N(i)c_{ij_r}c_{ik_s}S_{j_r k_s}. \quad (1)$$

Here c_{ij} are MO coefficients, S_{ij} is an overlap integral between orbitals j and k , $N(i)$ is the number of electrons on molecular orbital i .

The total overlap population is

$$n = \sum_{j_r, k_s} n(j_r, k_s). \quad (2)$$

According to Mulliken [22], the overlap population is a direct counterpart of the covalent binding energy.

3.2. Chosen geometrical configurations and bond distances

The electronic structures of $[MCl_6]^-$, $[MOCl_4]^-$, $[M(OH)_2Cl_4]^-$, $[MOCl_5]^{2-}$ (M = Nb, Ta, Ha, and Pa) have been calculated for interatomic distances metal-ligand changing in quite a range: from short bond lengths realized in the solid state to sums of the ionic radii (IR). To have the possibility to compare the results of the calculations we had to assume a definite scheme of changing these distances from one compound to another.

For the anions $[NbCl_6]^-$ and $[TaCl_6]^-$ (O_h symmetry) the bond lengths have been varied from 2.33 and 2.37 Å (for the solid state, see Sec. 2) to the sums of the ionic radii [23] equal to 2.45 Å. To judge about the right choice of the distances M–Cl the energies of the first charge-transfer transitions have been calculated via the transition-state procedure for the $[MCl_6]^-$ (M = Nb, Ta) ions and compared with experimental data [24] for their solutions in acetonitrile. The

Table 1. Electronic absorption spectra and assignments for the $[\text{NbCl}_6]^-$ and $[\text{TaCl}_6]^-$ (in cm^{-1})

Compound	$R_{\text{M-Cl}}, \text{\AA}$	$1t_{1g} \rightarrow 2t_{2g}$	$2t_{1u} \rightarrow 2t_{2g}$	Reference
$[\text{NbCl}_6]^-$...	28900	31800	Exp. [24(a)]
	...	28700	31700	Exp. [24(b)]
	2.33	24874	27442	Present
	2.37	23622	26054	calculations
$[\text{TaCl}_6]^-$...	34800	38000	Exp. [24(a)]
	...	29900	34900	Exp. [24(b)]
	2.33	28958	31574	Present
	2.37	27500	30242	calculations

comparison of the calculated and experimental values is given in Table 1.

The experimental electron transition bands undergo a small red shift, when excess of the solvent is added, due to solvolysis [24]. As a rule the energies of the charge-transfer transitions decrease with increasing distances metal-ligand. From Table 1 one can see that for the shortest bond length (2.33 \AA) realized in the solid state the energies are still less than the experimental values. So, the distances in solutions should not be larger than 2.33 and 2.37 \AA for Nb and Ta complexes, respectively. Taking into account the red shift, the first charge bands in the solutions will hardly be lower in energy than 23622 and 27500 cm^{-1} for Nb and Ta anions, respectively. Thus, these distances (2.33 and 2.37 \AA) are the shortest possible and they can be accepted as a reference point in the present calculations. The Ha-Cl distance in $[\text{HaCl}_6]^-$ was assumed to be 2.45 and 2.41 \AA . The former value was taken in accordance with differences in IR between Ha and Nb/Ta obtained on the basis on the MCDF calculations [2]. The latter value takes into account a possible relativistic contraction of the bond lengths. The Pa-Cl separation in $[\text{PaCl}_6]^-$ was taken in accordance with the differences in IR [23] between Nb/Ta and Pa.

For $[\text{NbOCl}_4]^-$ complexes, experimental bond lengths [14] were taken (see Sec. 2) and a geometrical configuration as a square pyramid with C_{4v} symmetry. For complexes of the other elements of this formula the same geometry was assumed and bond lengths were estimated in accordance with the differences in IR. The Pa=O separation was taken from the solid state structural data for $[\text{PaOCl}_5]^{2-}$.

Geometrical configuration of $[\text{M}(\text{OH})_2\text{Cl}_4]^-$ ($\text{M} = \text{Nb, Ta, Ha}$) was taken as a distorted octahedron with the OH-groups in a cis-position to each other. For $[\text{Pa}(\text{OH})_2\text{Cl}_4]^-$ a square bipyramide was chosen with OH groups in a trans-position to each other. The bond lengths are listed in Table 2.

For $[\text{NbOCl}_5]^{2-}$ (a distorted octahedron of C_{4v} symmetry), the Nb=O distance was taken from the experimental data (see Sec. 2), but the M-Cl one

equal to 2.15 \AA seems to be too short for the ion in solution.

The estimates of the bond lengths for the $[\text{MOCl}_5]^{2-}$ complexes in solutions have been made taking into account a pronounced trans-effect in these compounds, which makes the M-Cl bonds not equivalent (Fig. 1). Thus, in octahedral complexes of d elements a chlorine atom in the trans-position to oxygen is at a longer M-Cl separation than the equatorial chlorines as, e.g., in $[\text{MoOCl}_5]^{2-}$ where the difference in bond lengths between an axial and an equatorial chlorine is 0.15–0.25 \AA . In analogy with the molybdenum oxychloride complex we assume a geometrical configuration with elongated M-Cl_{eq} bond for Nb, Ta, and Ha complexes.

In actinide complexes the trans-effect is opposite to that of the d element compounds (Fig. 1). Here the axial chlorine atom in a trans-position to oxygen has a shorter separation from the central metal atom than the equatorial chlorines. E.g., in $[\text{UOCl}_5]^-$ the distance $\text{U-Cl}_{\text{ax}} = 2.43 \text{\AA}$ and $\text{U-Cl}_{\text{eq}} = 2.53 \text{\AA}$. Having this in mind, the bond lengths in $[\text{PaOCl}_5]^{2-}$ were estimated on the basis of the solid state structural data with the trans-effect being similar to that of $[\text{UOCl}_5]^-$.

The different trans-effect in the actinide and d -element compounds is explained by different ordering of vacant MOs in these systems [25]. The different ordering of the MOs causes different vibrational modes (T_{1u} in d elements and E_g in the actinides) to be active thus giving rise to the different distortions of the octahedral systems.

The list of the bond lengths used for the calculations is presented in Table 2. (The equal M-Cl distances in different types of complexes $[\text{MCl}_6]^-$, $[\text{MOCl}_4]^-$, and $[\text{MOCl}_5]^{2-}$ of one element makes it possible to compare qualitatively results of the calculations, while additional calculations were also performed for different M-Cl separations).

4. Results of the calculations and discussion

4.1. The structure of energy levels and effective charges

The energy level diagrams for the $[\text{MOCl}_4]^-$ ($\text{M} = \text{Nb, Ta, Ha, and Pa}$) complexes are typical of all the oxyhalide complexes of these elements (Fig. 2). The highest occupied levels are MOs of predominantly $3p(\text{Cl})$ character and separated from them by an energy gap ΔE are vacant levels of predominantly $d(\text{metal})$ character. All the complexes of the d elements (Nb, Ta, and Ha) show similar energy level ordering, while Pa has a somewhat different energy level scheme corresponding to the $5f, 6d(\text{metal})$ -ligand bonding.

The crystal-field splitting of the valence d orbitals in $[\text{MOCl}_4]^-$ complexes increases in the direction $\text{Nb} \rightarrow \text{Ta} \rightarrow \text{Ha}$. A relative lowering of the highest unoccupied levels in $[\text{HaOCl}_4]^-$ is due to a large con-

Table 2. Bond lengths metal–ligand assumed for the present calculations (in Å)

Distance	[NbCl ₆] [−]	[TaCl ₆] ^{−3}	[HaCl ₆] [−]		[PaCl ₆] [−]		
M–Cl	2.37	2.37	2.41 ^a	2.45	2.51		

Distance	[NbOCl ₄] [−]	[TaOCl ₄] ^{−e}	[HaOCl ₄] [−]		[PaOCl ₄] [−]		
M=O	1.70	1.70	1.74 ^a	1.78	1.74 ^b	2.05 ^c	2.11 ^d
M–Cl	2.37	2.37	2.41 ^a	2.45	2.59 ^b	2.51 ^c	2.15 ^d

Distance	[Nb(OH) ₂ Cl ₄] [−]	[Ta(OH) ₂ Cl ₄] ^{−e}	[Ha(OH) ₂ Cl ₄] [−]	[Pa(OH) ₂ Cl ₄] [−]
M–O _{eq}	2.01	2.01	2.09	2.15
O–H	1.02	1.02	1.02	1.02
M–Cl _{eq}	2.37	2.37	2.45	2.51

Distance	[NbOCl ₅] ^{2−}	[TaOCl ₅] ^{2−}	[HaOCl ₅] ^{2−e}		[PaOCl ₅] ^{2−}		
M=O	1.97	1.97	2.01 ^a	2.05	1.74 ^b	2.05 ^c	2.11 ^d
M–Cl _{eq}	2.34	2.34	2.37 ^a	2.42	2.60 ^b	2.53 ^c	2.53 ^d
M–Cl _{ax}	2.49	2.49	2.52 ^a	2.57	2.52 ^b	2.43 ^c	2.43 ^d

^a Values with relativistic bond contraction. ^b Experimental values [17] for [PaOCl₅]^{2−}. ^c In accordance with the differences in IR between Pa and Nb(Ta), but with a shorter Pa=O bond. ^d On the basis of the differences in IR. ^e The calculations have also been done for the tantalum complexes with longer Ta–Cl/O distances than in the corresponding niobium complexes which can be true for solutions. Thus, e.g., for [TaOCl₅]^{2−} some results are presented for M–Cl_{eq} = 2.35 and M–Cl_{ax} = 2.55 Å.

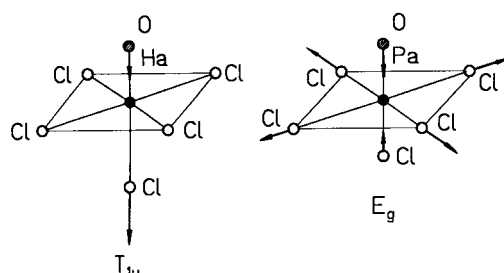


Fig. 1. Different trans-effect in the octahedral complexes of the *d* elements and actinides (T_{1u} and E_g are different vibrational modes).

tribution of the 7*s*-AO which is relativistically stabilized.

A detailed analysis of the MO composition and bonding in halides and oxyhalides of the elements under consideration has been given in our earlier works [19–21]. Here we will pay our attention only to the analysis of the tendency of a metal to form a particular coordination or a type of a complex, and the involvement of the metal valence orbitals in the bonding.

In Table 3 the values of the effective charges on atoms are given as a result of the present calculations. As in the corresponding halides MCl₅ and oxyhalides MOCl₃ (M = Nb, Ta, Ha, and Pa) [19–21], hahnium shows the lowest ionicity in each series of the compounds under consideration. Protactinium in its anionic complexes with oxygen is less ionic than Ta (and Nb) in contrast to the pure halides MCl₅,

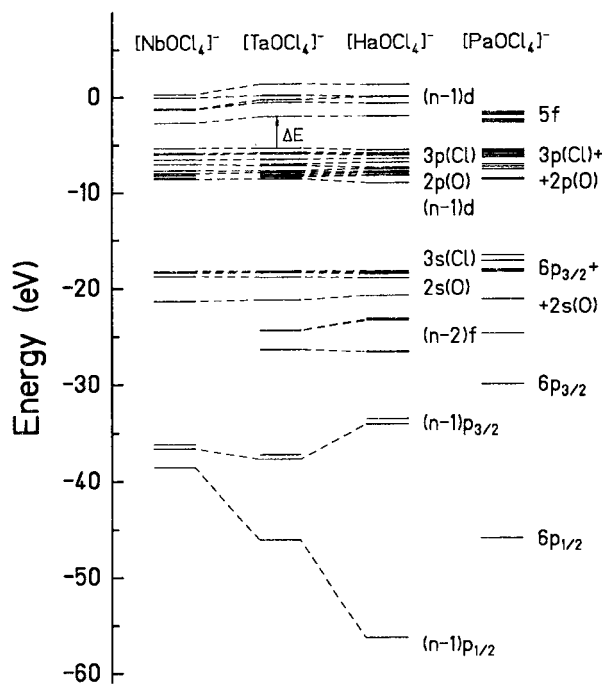


Fig. 2. Energy eigenvalues for [MOCl₄][−] (M = Nb, Ta, Ha, and Pa).

oxyhalides MOCl₃ and the hexahalide complexes [MCl₆][−].

It is worth noting here that the pure chloride complexes [MCl₆][−] are less ionic than the oxychloride ones.

Table 3. Effective charges on the metal atoms and ligands for $[\text{MCl}_6]^-$, $[\text{MOCl}_4]^-$, $[\text{M}(\text{OH})_2\text{Cl}_4]^-$ and $[\text{MOCl}_5]^{2-}$

Q	$[\text{NbCl}_6]^-$	$[\text{TaCl}_6]^-$	$[\text{HaCl}_6]^-$ ^a	$[\text{PaCl}_6]^-$
Q_{M}	0.69	0.69	0.56	0.75
Q_{Cl}	-0.28	-0.28	-0.26	-0.29

Q	$[\text{NbOCl}_4]^-$	$[\text{TaOCl}_4]^-$	$[\text{HaOCl}_4]^-$ ^b	$[\text{PaOCl}_4]^-$ ^c
Q_{M}	0.85	0.89	0.72	0.87
Q_{O}	-0.40	-0.43	-0.42	-0.44
Q_{Cl}	-0.36	-0.36	-0.32	-0.36

Q	$[\text{Nb}(\text{OH})_2\text{Cl}_4]^-$	$[\text{Ta}(\text{OH})_2\text{Cl}_4]^-$	$[\text{Ha}(\text{OH})_2\text{Cl}_4]^-$ ^b	$[\text{Pa}(\text{OH})_2\text{Cl}_4]^-$ ^c
Q_{M}	0.98	1.01	0.89	0.92
$Q_{\text{O}_{\text{eq}}}$	-0.60	-0.61	-0.60	-0.59
$Q_{\text{Cl}_{\text{eq}}}$	-0.36	-0.36	-0.34	-0.34
$Q_{\text{H}_{\text{ax}}}$	0.32	0.34	0.34	0.31

Q	$[\text{NbOCl}_5]^{2-}$	$[\text{TaOCl}_5]^{2-}$	$[\text{HaOCl}_5]^{2-}$ ^d	$[\text{PaOCl}_5]^{2-}$ ^e
Q_{M}	0.69	0.76	0.61	0.53
Q_{O}	-0.47	-0.51	-0.49	-0.51
$Q_{\text{Cl}_{\text{ax}}}$	-0.50	-0.50	-0.47	-0.37
$Q_{\text{Cl}_{\text{eq}}}$	-0.43	-0.43	-0.39	-0.41

^a For $R_{\text{M-Cl}} = 2.41 \text{ \AA}$. ^b For $R_{\text{M-O}}/R_{\text{M-Cl}} = 1.78/2.45 \text{ \AA}$. ^c For $R_{\text{M-O}}/R_{\text{M-Cl}} = 1.74/2.59 \text{ \AA}$. ^d For $R_{\text{M-O}}/R_{\text{M-Cl}_{\text{eq}}}/R_{\text{M-Cl}_{\text{ax}}} = 2.05/2.42/2.57 \text{ \AA}$. ^e For $R_{\text{M-O}}/R_{\text{M-Cl}_{\text{eq}}}/R_{\text{M-Cl}_{\text{ax}}} = 1.74/2.53/2.43 \text{ \AA}$.

4.2. Analysis of the partial overlap population and bonding

To answer the question why an element forms this and not the other type of complex in solution is a difficult task. The complex formation depends on many parameters, such as equilibrium constants, concentrations, solvation, etc. and particular conditions of an experiment. Nevertheless, we will try to analyze this process considering only the tendency of a metal to form covalent bonding with particular ligands and their number (or coordination), and to understand the reasons for that, namely, the preference of a metal to form pure halide or oxyhalide complexes. To make a qualitative comparison in terms of the overlap population, we will consider complexes with the same high coordination number which are formed in the concentrated HCl solutions. These are $[\text{MCl}_6]^-$ and $[\text{MOCl}_5]^{2-}$ ($\text{M} = \text{Nb, Ta, Ha, and Pa}$) anions.

For the beginning, we will consider the involvement of the metal valence orbitals in bonding with the valence orbitals of the ligands. This can be done on the basis of the partial overlap population data obtained as a result of the present MO calculations in accordance with Eq. (1). These data are presented in Table 4 and 5.

From Table 4, one can see that the involvement of the d orbitals in bonding both with oxygen and chlorine is smoothly increasing in going from niobium to tantalum and to hahnium complexes. The energetic destabilization of these orbitals as a secondary re-

lativistic effect does not result in their lower overlap with valence ligand orbitals when going from Ta to Ha. Being relatively destabilized in energy, these orbitals have a larger expansion with increasing atomic number and hence the larger overlap with ligands. Because the energetic destabilization and spatial extension act in opposite directions the total overlap $d(\text{metal})$ -ligand increases only slightly in going from Nb to Ta and to Ha. The $np_{1/2}$ metal orbitals give increasing overlap along the series Nb, Ta, and Ha due to their relativistic stabilization with increasing atomic number.

An interesting behaviour show the $np_{3/2}(\text{metal})$ orbitals. The destabilization of this orbital as a secondary relativistic effect in the hahnium compound is so that the overlap of the hahnium atom with chlorines is even less than in the niobium complex. The ns orbital behaviour is also very interesting. In going from Nb to Ta and to Ha compounds, the overlap $ns(\text{M})-\text{O}$ increases smoothly due to the relativistic stabilization of the ns orbitals, while the $ns(\text{M})-\text{Cl}$ overlap increases to a larger extent in going from Nb to Ta than in going from Ta to Ha. Obviously, in hahnium compounds the short $\text{Ha}=\text{O}$ bond with larger (compared to the single bonds) $7s(\text{metal})$ character still has essential electron density on it, while in case of single bonds with big ligands like Cl the relativistic contraction of the $7s$ orbitals make them even less accessible for valence Cl orbitals than the $6s$ orbitals in the case of Ta.

Table 4. Partial overlap populations of the valence metal orbitals with ligands for $[\text{MOCl}_5]^{2-}$

$n(j_r, k_s)$	$[\text{NbOCl}_5]^{2-}$	$[\text{TaOCl}_5]^{2-}$	$[\text{HaOCl}_5]^{2-a}$	$[\text{PaOCl}_5]^{2-b}$
$ns_{1/2}-\text{O}$	0.06	0.08	0.11	0.05
$ns_{1/2}-5\text{Cl}$	0.33	0.40	0.44	0.25
$ns_{1/2}(\text{tot})$	0.39	0.48	0.55	0.30
$(n-1)d_{3/2}-\text{O}$	0.28	0.28	0.29	0.23
$(n-1)d_{3/2}-5\text{Cl}$	0.51	0.54	0.55	0.66
$(n-1)d_{3/2}(\text{tot})$	0.79	0.82	0.84	0.89
$(n-1)d_{5/2}-\text{O}$	0.42	0.43	0.44	0.36
$(n-1)d_{5/2}-5\text{Cl}$	0.82	0.84	0.88	0.95
$(n-1)d_{5/2}(\text{tot})$	1.24	1.27	1.32	1.31
$(n-1)d-\text{O}$	0.70	0.71	0.73	0.59
$(n-1)d-5\text{Cl}$	1.33	1.38	1.43	1.61
$np_{1/2}-\text{O}$	0.06	0.07	0.08	0.06
$np_{1/2}-5\text{Cl}$	0.20	0.25	0.30	0.17
$np_{1/2}(\text{tot})$	0.26	0.32	0.38	0.23
$np_{3/2}-\text{O}$	0.10	0.14	0.12	0.10
$np_{3/2}-5\text{Cl}$	0.39	0.41	0.33	0.25
$np_{3/2}(\text{tot})$	0.49	0.55	0.45	0.35
$np-\text{O}$	0.16	0.21	0.20	0.16
$np-5\text{Cl}$	0.59	0.61	0.63	0.42

^a For $R_{\text{M-O}}/R_{\text{M-Cl}_{\text{eq}}}/R_{\text{M-Cl}_{\text{ax}}} = 2.05/2.42/2.57 \text{ \AA}$. ^b For $R_{\text{M-O}}/R_{\text{M-Cl}_{\text{eq}}}/R_{\text{M-Cl}_{\text{ax}}} = 2.11/2.53/2.43 \text{ \AA}$. For $[\text{PaOCl}_5]^{2-}$: $n(5f_{5/2}-\text{O}) = 0.13$; $n(5f_{7/2}-\text{O}) = 0.17$; $n(5f_{5/2}-\text{Cl}) = 0.48$; $n(5f_{7/2}-\text{Cl}) = 0.27$.

Table 5. Partial overlap populations of the valence metal orbitals with ligands for $[\text{MCl}_6]^-$

$n(j_r, k_s)$	$[\text{NbCl}_6]^-$	$[\text{TaCl}_6]^-$	$[\text{HaCl}_6]^{-a}$
$ns_{1/2}-6\text{Cl}$	0.36	0.49	0.54
$(n-1)d_{3/2}-6\text{Cl}$	0.84	0.84	0.89
$(n-1)d_{5/2}-6\text{Cl}$	1.27	1.28	1.35
$np_{1/2}-6\text{Cl}$	0.23	0.34	0.38
$np_{3/2}-6\text{Cl}$	0.42	0.48	0.35
$np-\text{O}$	0.16	0.21	0.20
$np-5\text{Cl}$	0.59	0.61	0.63

^a For $R_{\text{M-Cl}} = 2.41 \text{ \AA}$.

This is especially well seen in case of the pure chloride complexes (Table 5). In going from $[\text{NbCl}_6]^-$ to $[\text{TaCl}_6]^-$ the overlap ns -chlorine increases by 0.12 while in going from $[\text{TaCl}_6]^-$ to $[\text{HaCl}_6]^-$ it increases only by 0.05. The $np_{3/2}-\text{Cl}$ overlap in the hahnium compound is again smaller than in the niobium case.

4.3. Trans-effect in the $[\text{MOCl}_5]^{2-}$ complexes

The change in the AO's contributions to bonding from Nb to Ha changes the relationship between covalent bonding of the metals with equatorial chlorines and the bonding with axial chlorine, $n(\text{M}-\text{Cl}_{\text{eq}})/n(\text{M}-\text{Cl}_{\text{ax}})$. In $[\text{NbOCl}_5]^{2-}$ $n(\text{Nb}-\text{Cl}_{\text{eq}}) < n(\text{Nb}-\text{Cl}_{\text{ax}})$, in tantalum complex $n(\text{Ta}-\text{Cl}_{\text{ax}}) \simeq n(\text{Ta}-\text{Cl}_{\text{eq}})$ and in the hahnium oxychloride anion $n(\text{Ha}-\text{Cl}_{\text{eq}}) > n(\text{Ha}-\text{Cl}_{\text{ax}})$. The change in the relative values of the

covalent bonding $n(\text{M}-\text{Cl}_{\text{eq}})/n(\text{M}-\text{Cl}_{\text{ax}})$ in going from Nb to Ta will influence the trans-effect in these complexes. Increase in the covalent bonding $\text{M}-\text{Cl}_{\text{eq}}$ in Ha complex will result in decreasing the trans-effect on the coordinate $\text{Cl}_{\text{ax}}-\text{Ha}-\text{O}$, so that the influence of Cl_{ax} on oxygen will be diminished. As a consequence, the oxygen atom will be bound stronger and less easily substituted by Cl^- or another anion than the oxygen atoms in Ta or in Nb oxypentahalide complexes. (In the other words, the stronger the cis-influence of Cl_{eq} , the weaker the trans-effect, the stronger bound is oxygen).

Let us consider now the trans-effect as influence of Cl_{ax} on the oxygen atom for the entire series $[\text{MOCl}_5]^{2-}$. Correlation between the covalency of a bond and the trans-activity of the corresponding ligand is well known [26]. The stronger $\text{Cl}_{\text{ax}}-\text{M}$ bonding, the more trans-active is Cl_{ax} . A large overlap $\text{Cl}(p_x, p_y)-\text{M}(d_{xz}, d_{yz})$ forming π -bonding results in shifting the electron density from the $\text{M}=\text{O}$ bond to the $\text{M}-\text{Cl}_{\text{ax}}$ one and making the $\text{M}=\text{O}$ bonding nearly ionic. This makes substitution of oxygen by Cl^- easier. (The trans-influence of Cl_{ax} decreases the activation energy of the intermediate "activated complex", resulting in the trans-substitution).

From Table 6, one can see that out of the entire series Ta has the highest covalency (overlap population) of the bond $\text{M}-\text{Cl}_{\text{ax}}$ in $[\text{TaOCl}_5]^{2-}$. Thus the substitution of oxygen in $[\text{TaOCl}_5]^{2-}$ would be the most easily reached. (From Table 3 one can see, that the most ionic oxygen is in the tantalum complex.) Besides, the substitution of the oxygen atom by Cl^- in $[\text{TaOCl}_5]^{2-}$ would result in the gain in the total covalent bonding in $[\text{TaCl}_6]^-$ compared to the

Table 6. Total overlap population data for $[\text{MCl}_6]^-$ and $[\text{MOCl}_5]^{2-}$ complexes

$n(\text{M}-\text{L})$	$[\text{NbCl}_6]^-$	$[\text{TaCl}_6]^-$ ^a	$[\text{HfCl}_6]^-$ ^b	$[\text{PaCl}_6]^-$
M-Cl	0.42	0.50	0.49	0.42
M-6Cl(tot)	2.52	2.97	2.95	2.51

$n(\text{M}-\text{L})$	$[\text{NbOCl}_5]^{2-}$	$[\text{TaOCl}_5]^{2-}$ ^c	$[\text{HfOCl}_5]^{2-}$ ^d	$[\text{PaOCl}_5]^{2-}$ ^e
M=O	0.78	0.88	0.92	0.83
M-Cl _{eq}	0.34	0.39	0.42	0.36
M-Cl _{ax}	0.36	0.40	0.36	0.28
M-L(tot)	2.51	2.85	2.96	2.57

^a For comparison in the complex of Ta the M-Cl distances are the same as for Nb. The larger distances Ta-Cl give even higher overlap population. ^b For 2.45 Å. ^c For $R_{\text{M-O}}/R_{\text{M-Cl}_{\text{eq}}}/R_{\text{M-Cl}_{\text{ax}}} = 1.97/2.35/2.55$ Å. ^d For $R_{\text{M-O}}/R_{\text{M-Cl}_{\text{eq}}}/R_{\text{M-Cl}_{\text{ax}}} = 2.05/2.42/2.57$ Å. ^e For $R_{\text{M-O}}/R_{\text{M-Cl}_{\text{eq}}}/R_{\text{M-Cl}_{\text{ax}}} = 2.11/2.53/2.43$ Å.

oxyhalide complex. This can be seen when comparing the total overlap populations of these two complexes (Table 6).

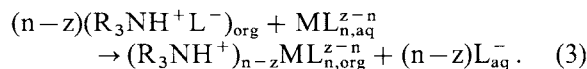
In the niobium and hafnium complexes the trans-effect is weaker, than in the tantalum one, and oxygen is stronger bound. The weakest trans-effect will be in the protactinium complex, where the covalency of the bond M-Cl_{ax} is the smallest.

4.4. Covalent bonding in the anionic complexes

Finally, the advantage of an element to form oxyhalide or pure halide complex in terms of the covalent bonding can be seen from Table 6. There, in the $[\text{MOCl}_5]^{2-}$ compounds the total overlap increases from Nb to Ta and to Hf complexes, while for the series of $[\text{MCl}_6]^-$ complexes this is not the case. The covalency increases from niobium to tantalum hexahalide anions, while from Ta to Hf there is no increase in bonding with six chlorines. The small overlap of the ns and $np_{3/2}$ orbitals with chlorines leads to the total overlap metal-ligand in the hafnium complex being not larger than in the tantalum one. Comparing overlap populations in $[\text{MCl}_6]^-$ and $[\text{MOCl}_5]^{2-}$, one can see that tantalum shows the clear preference to form pure halide complexes, while for niobium and hafnium the trends to form oxyhalide and halide complexes are nearly equal (for Hf there is even more pronounced trend to form oxyhalide species). Protactinium would form oxyhalide complexes rather than the hexahalide ones.

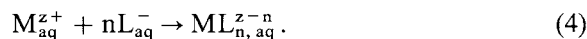
5. Extraction of the group 5 elements by anion exchange with aliphatic amines

The equilibrium of the extraction of a ML_n^{z-n} by a long-chain aliphatic amine from an aqueous phase (when the amine R_3N is previously equilibrated with acid HL) can be expressed via anion exchange as follows [27]:



The complex ion in the aqueous phase and an oppositely charged ion present in either the aqueous or the organic phase.

Numerous studies [9] on the extractability of metal chlorides from HCl or HCl+HF solutions show that polyvalent metals, readily forming anionic chloro complexes, exhibit the highest distribution ratios, followed by metals forming oxyanions. Thus, first of all the order of metal extractability is what should be expected from the tendency of the metals to form anionic chloro complexes with lowest charge



Since Ta has the highest tendency to form pure halide mono-charged complex $[\text{TaCl}_6]^-$ (or $[\text{TaCl}_5\text{F}]^-$ in HCl+HF solutions) (see Table 6), its extractability from the HCl (or HCl+HF) solutions is the highest among the metals under consideration. Experiments [4-6] clearly show this. (We note here, that quite often [9] Ta shows nearly no extractability from pure HCl into the organic phase due to a very strong hydrolysis, while in the HCl+HF solutions the hydrolysis is suppressed by some coordination of F^- ligands and Ta is very well extracted into the organic phase).

Another fact explaining a high extractability of $[\text{TaCl}_6]^-$ (and of $[\text{NbCl}_6]^-$) complex ions is their higher covalency in comparison with the corresponding oxyhalide ions (see Table 3 and 6). Since the interaction of $[\text{MCl}_6]^-$ ion with the surrounding molecules of the aqueous or organic phase is due to the hydrophobic part of Cl, the lower effective charge on $\text{Cl}^{\delta-}$ in $[\text{MCl}_6]^-$ complex compared to the oxyhalide ones facilitates its transfer from the aqueous to organic phase (to the medium with lower dielectric constant). (Provided $[\text{HfCl}_6]^-$ is formed at some special conditions, its extractability will be higher than that of the oxyhalide ions.)

Another important aspect is that highly symmetric $[\text{MCl}_6]^-$ ions have no dipole moments, while any asymmetric angle-structure oxyhalide complexes of d

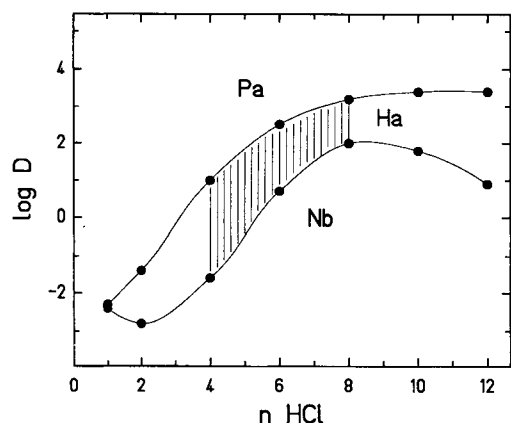


Fig. 3. The distribution coefficients between the TIOA and aqueous HCl phase as a function of HCl concentration. The D for Pa and Nb are literature data [9]. The $D(\text{Ha})$ values are expected to be in the area between the D values for Pa and Nb.

elements have dipole moments which favour their stay in the medium with high dielectric constant. Thus, all these above mentioned factors contribute to the high extractability of the tantalum halide ion into the organic phase.

To estimate the extractability of the same sort of complexes, like $[\text{MOCl}_5]^{2-}$, $[\text{MOCl}_4]^-$ or $[\text{M}(\text{OH})_2\text{Cl}_4]^-$, under the same conditions one can apply Born's theory of solubility [28] to the process of transfer of an ion from the aqueous to the organic phase and Bjerrum's theory of the ionic association [29] for the ionic association in the organic phase.

Results obtained by application of these theories are overall simplified because they take into consideration only electrostatic interaction. In real extraction systems the nature of the organic phase should be taken into account, i.e. the structure and size of the organic base, and particular conditions of an experiment. In practice, however, the electrostatic interaction in the ion associating, the size and degree of hydration of the ions, allow to make the right estimates of the extraction.

Thus, in accordance with Born's theory for the process of the transfer of the same type of complexes from the aqueous into organic phase one has to know finally the sizes of the extracted species to estimate the partition between the two phases with the partition coefficient being expressed as follows

$$P = \frac{C_{\text{org}}}{C_{\text{aq}}} = \frac{\gamma_{\text{aq}}}{\gamma_{\text{org}}} \exp \left[\frac{Ne^2 Z_i^2}{2RT r_i} \left(\frac{1}{\epsilon_{\text{org}}} - \frac{1}{\epsilon_{\text{aq}}} \right) \right]. \quad (5)$$

Here γ_{org} and γ_{aq} are activity coefficients of the solute in the organic and aqueous phases, and normally $\epsilon_{\text{org}} < \epsilon_{\text{aq}}$.

Since Nb, Pa, and Ha show similar trends to form $[\text{MOCl}_5]^{2-}$ complexes in terms of the bonding with the ligands, and assuming their formation constants are of the same order of magnitude, we will try to estimate their extractability as a function of their size.

The size of these species can be estimated on the basis of the IRs of the constituent simple ions. Finally, the differences in their sizes are determined by the differences in the IRs of the metals. The IR of Nb and Pa are 0.64 and 0.78 Å, respectively [23]. MCDF calculations [2] give the estimate of the IR of Ha as 0.74 Å. Thus, r_i of the $[\text{MOCl}_5]^{2-}$ ions would be $\sim 4.17, 4.25$ and 4.31 Å for Nb, Ha, and Pa respectively. The partition of the anionic species under consideration between the organic and aqueous phases will be then

$$P_{[\text{NbOCl}_5]^{2-}} < P_{[\text{HaOCl}_5]^{2-}} < P_{[\text{PaOCl}_5]^{2-}}. \quad (6)$$

Similarly, at lower HCl concentrations the partition coefficients will be

$$P_{[\text{NbOCl}_4]^-} < P_{[\text{HaOCl}_4]^-} < P_{[\text{PaOCl}_4]^-} \quad (7)$$

and

$$P_{[\text{Nb}(\text{OH})_2\text{Cl}_4]^-} < P_{[\text{Ha}(\text{OH})_2\text{Cl}_4]^-} < P_{[\text{Pa}(\text{OH})_2\text{Cl}_4]^-}. \quad (8)$$

Experimental [9] distribution coefficients for Nb and Pa at medium and high concentrations are shown in Fig. 3. The expected positions of the distribution coefficient for the oxyhalide complexes of Ha are shown as a shaded area.

Extraction from the mixed HCl + HF solutions has obviously more complicated character what concerns defining particular types of complexes. Pa has an enormous decrease of extractability in the presence of fluoride ion [4, 30, 31]. This is due to the fact that Pa has a greater tendency to complex with fluoride ions than chloride ones, and in the presence of even low concentration of fluoride ions, they form multiple charged complexes $[\text{PaF}_7]^{2-}$ or $[\text{PaF}_8]^{3-}$. The decrease in the extraction of Pa from HF + HCl solutions was explained [31] to be a reason of high negative charges of these anions. We would like to add here, that the lower extraction of the fluoride complexes can be also explained as reason of their higher ionicity compared to the chloro complexes and their smaller sizes.

In the experiments [30] position of the distribution coefficient of Ha was found below Nb but higher than that of Pa. That might be also explained by the formation of multicharged mixed chloro-fluoro ions, like, e.g. $[\text{HaOF}_x\text{Cl}_y]^{x+y-3}$ or $[\text{HaF}_x\text{Cl}_y]^{x+y-5}$. In a more clear case of the extraction from pure HCl solutions new experiments will hopefully show a position of Ha from which one can conclude about types of complexes formed.

Let us consider now the association of the anionic complexes in the organic phase with the organic cation: $[(\text{R}_3\text{NH})_2(\text{MOCl}_5)]$. According to Bjerrum's theory [29], the value of association constant K_{ass} of a pair of oppositely charged ions can be calculated as a function of the dielectric constant, ϵ_{org} , ionic charges Z_1 and Z_2 , and the distance of closest approach of the ions $q = r_1 + r_2$:

$$K_{\text{ass}} = \frac{4\pi N}{1000} \left(\frac{Z_1 Z_2 e^2}{\epsilon_{\text{org}} kT} \right)^2 Q(b), \quad (9)$$

where $Q(b) = \int_2^b e^y y^{-4} dy$, $y = e^2 / r \epsilon_{\text{org}} kT$ and $b = e^2 / q \epsilon_{\text{org}} kT$.

The free energy of the ion-associating is about one-half the difference in the electrostatic solvation energies, so that a considerable positive free energy of transfer remains.

According to Eq. (9) in an organic medium of a definite ϵ_{org} and at $T = \text{const.}$, K_{ass} depends only on the charge of an ion and the closest approach of the ion and organic cation, q . In case of $[\text{MOCl}_5]^{2-}$ anions of Nb, Ha and Pa in TIOA, the final dependence will be only on q .

The knowledge of q is important to judge about the ion-association in the organic phase. It was shown [32] that q is about 2 Å larger the simple sum of the ionic radii of the cation and anion $d = r_{\text{R}_3\text{NH}^+} + r_{[\text{MOCl}_5]^{2-}}$. (The anions under discussion form contact ion pairs with the organic cation R_3NH^+ , since the solvent is not basic and they have quite big sizes.) Besides, at a particular q there is a critical ϵ_c above which there is no association of the ions. (This can be seen from the graphs $\log K_{\text{ass}}$ vs. ϵ_{org} in Ref. [32], where starting with some ϵ_{org} at a particular distance between an organic cation and an anion, the value of $\log K_{\text{ass}}$ starts to be positive). The higher q , the lower is ϵ_c .

Assuming that the center of charge in R_3NH^+ is similar to that in $(\text{NH}_4)^+$, and having in mind that the real distance q is bigger than the distance d between the centers of charges in the dipole $\text{R}_3\text{NH}^+ \dots [\text{MOCl}_5]^{2-}$, the values of q for Nb, Ha, and Pa associated complexes can be estimated as 7.78, 7.85, and 7.92 Å, respectively. (The hydrogen bonding in $\text{R}_3\text{NH}^+ \dots [\text{MOCl}_5]^{2-}$ makes the distance q partially shorter.)

For q equal to ~ 8 Å, the critical value of the dielectric constant ϵ_c is equal to ~ 40 . Thus, in the medium with $\epsilon_c \geq 40$ there will be no association between the organic cation and the anions.

Using the estimates of q for the oxychloride anions of Nb, Ha, and Pa, the strength of the associated complexes at high HCl concentrations due to the electrostatic interaction will be:

$$K_{\text{ass}}(\text{NbOCl}_5^{2-}) > K_{\text{ass}}(\text{HaOCl}_5^{2-}) > K_{\text{ass}}(\text{PaOCl}_5^{2-}). \quad (10)$$

In analogy for the intermediate HCl molarities

$$K_{\text{ass}}(\text{NbOCl}_4^-) > K_{\text{ass}}(\text{HaOCl}_4^-) > K_{\text{ass}}(\text{PaOCl}_4^-), \quad (11)$$

$$K_{\text{ass}}[\text{Nb}(\text{OH})_2\text{Cl}_4^-] > K_{\text{ass}}[\text{Ha}(\text{OH})_2\text{Cl}_4^-] > K_{\text{ass}}[\text{Pa}(\text{OH})_2\text{Cl}_4^-]. \quad (12)$$

Beside the electrostatic interaction in the associated complexes, the hydrogen bonding $\text{R}_3\text{NH}^+ \dots [\text{OMCl}_5]^{2-}$ contributes to the strength of the association. In the series of $[\text{MOCl}_5]^{2-}$ ($M = \text{Nb, Ha, and Pa}$) the

strength of the hydrogen bonding will be proportional to the value of the effective charge on the oxygen atom in $[\text{MOCl}_5]^{2-}$. From Table 3 the q_0 in Nb, Ha, and Pa complexes are -0.47 , -0.49 , and -0.51 , respectively. Thus, the hydrogen bonding is the strongest in the protactinium associated complex and the weakest in the niobium one. Nevertheless the differences between q_0 of these anions are small and the hydrogen bonding is of the order of a fraction of eV. Finally, the total effect is determined by the electrostatic interaction so that the relation (10) is valid. (There might be also a partial charge transfer from oxygen of the anion to the hydrogen atom of the organic cation: $\text{R}_3\text{NH}^+ \dots \overset{\delta-}{\text{O}} - \text{MCl}_5^{2-}$, which will be also proportional to the value of q_0 . But the real distances in the associated complexes q are too big for the charge transfer to take place.)

The hydrogen bonding in $\text{R}_3\text{NH}^+ \dots [(\text{OH})_2\text{MCl}_4]^-$ is also proportional to the value of the effective charge on oxygen equal to -0.60 , -0.60 , and -0.59 for Nb, Ha, and Pa complexes, respectively. These values are nearly equal. Besides, the hydrogen bonding between these anions and the organic cation will be weaker than in case of the $[\text{MOCl}_5]^{2-}$ ions. Thus, relations (11) and (12) obtained on the basis of the pure electrostatic interaction will determine the ionic association at the medium HCl concentrations.

Application of Born's theory to the back-extraction (or the process of transfer of the ions from the organic to the aqueous phase) shows, that the smallest anion should be eluted first (Nb), then comes out the Ha anion, and then the Pa one.

6. Conclusions

Results of the DS DV calculations have shown the following.

a) $[\text{NbCl}_6]^-$ and $[\text{NbOCl}_5]^{2-}$ have nearly the same overlap metal-ligands, or in other words, the covalent bonding and the trends of Nb to form the pure hexahalide or oxyhalide complex ions with $\text{CN} = 6$ are equal. This statement is in line with experimental results [7, 14] which confirm the coexistence of the two forms at medium concentrations and only at concentrations > 12 M HCl the pure chloride complexes of Nb start to be predominant.

b) In contrast to the other elements, Ta has a much stronger overlap with six chlorines than when one chlorine is substituted by oxygen. Notwithstanding the fact that the Ta=O bond in $[\text{TaOCl}_5]^{2-}$ would have been stronger than Nb=O in $[\text{NbOCl}_5]^{2-}$, the coordination with six chlorines proves to be more favourable for Ta than for Nb. Besides, Ta in its pure halide form has the highest overlap population among all the complex ions.

c) Hahnium has similar overlap populations for both types of complexes and it has the strongest metal-oxygen bonding. If covalent bonding increases in going from $[\text{NbOCl}_5]^{2-}$ to $[\text{TaOCl}_5]^{2-}$ and to

$[\text{HaOCl}_5]^{2-}$ the covalent bonding with six chlorines in $[\text{MCl}_6]^-$ does not increase in going from $[\text{TaCl}_6]^-$ to $[\text{HaCl}_6]^-$. Thus, having the strongest tendency to bind oxygen, hahnium at medium HCl concentrations would preferably form $[\text{HaOCl}_5]^{2-}$ as Nb does. At higher concentrations one would think of the formation of rather $[\text{HaCl}_7]^{2-}$ like $[\text{PaCl}_7]^{2-}$ than $[\text{HaCl}_6]^-$ taking into account a larger IR of Ha (0.74 Å) in comparison with Ta (0.64 Å).

d) Pa in its oxyhalide complex has a rather strong bond Pa=O and the overlap population in $[\text{PaOCl}_5]^{2-}$ is slightly larger than in $[\text{PaCl}_6]^-$. Thus at HCl concentrations 6–7 M the former species are predominant, while at higher concentrations Pa starts to form pure halide complexes. Having an IR even larger than Ha, protactinium would rather form pure halide complexes with coordination number higher than 6 ($[\text{PaCl}_7]^{2-}$, $[\text{PaCl}_8]^{3-}$).

The highest trans-activity of Cl_{ax} in $[\text{TaOCl}_5]^{2-}$, or the largest covalency of the bond M– Cl_{ax} out of the entire series $[\text{MOCl}_5]^{2-}$ (M = Nb, Ta, Ha, and Pa), makes the Ta=O bonding weaker compared to the M=O ones in the complexes of the other elements and is the reason of the easier substitution of oxygen by chlorine. The substituted complex $[\text{TaCl}_6]^-$ has a higher covalency compared to $[\text{TaOCl}_5]^{2-}$. A strong cis-effect of Cl_{eq} in hahnium anion makes the bonding Ha=O stronger than that in Nb and Ta complexes.

Thus, the results of the calculations show qualitatively the trends found in the experiments: there is a specific position of Ta in the group and a tendency of Pa and Ha to form rather oxyhalide complexes $[\text{MOCl}_5]^{2-}$ or pure halide ones at high HCl concentrations with high coordination numbers ($[\text{MCl}_7]^{2-}$). This might be also an explanation of the experiments [6], where Ha was found to have a preference to form multicharged anionic complexes.

The specific position of Ta in the group determines the high extractability of its pure halide complexes from HCl+HF solutions to the organic medium due to their higher stability, higher covalency and lower charge compared to the oxyhalide complexes.

For the oxyhalide complexes of Nb, Pa, and Ha of the same chemical composition, Born's theory of ionic solvation gives the following succession of the partition coefficients:

$$P_{\text{Nb}} < P_{\text{Ha}} < P_{\text{Pa}}.$$

The strength of the ionic association in the organic phase for the associated complexes $(\text{R}_3\text{NH}^+)_2\text{-(MOCl}_5)$ and $(\text{R}_3\text{NH}^+)[\text{M(OH)}_2\text{Cl}_4]$ is

$$K_{\text{ass}}(\text{Nb}) > K_{\text{ass}}(\text{Ha}) > K_{\text{ass}}(\text{Pa}).$$

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