

Theoretical Predictions of Properties and Chemical Behavior of Superheavy Elements

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Fully relativistic electronic structure calculations have been performed for gas phase and aqueous phase compounds of elements 104 through 108. Based on these calculations, volatility and complex formation, as well as trends in these properties, have been predicted. The transactinide compounds were shown to exhibit properties very similar to those of the lighter homologs in the respective chemical groups. Some deviations from the observed trends were established.

1. Introduction

Fast progress in experimental investigations of chemical properties of the heaviest elements gives further impact to theoretical studies. Most of them are aimed at prediction of chemical behavior in sophisticated and expensive experiments with single atoms.

Recently, elements 107 (Bh)¹ and 108 (Hs)² were chemically identified using gas-phase chromatography techniques. They were shown to form BhO_3Cl and HsO_4 in analogy with lighter elements in the chemical groups Re and Os, respectively. Besides, the behavior of Rf and Sg which had already been characterized chemically has meanwhile been further studied in more detail. In some cases, deviations from trends in properties found for lighter homologs in the groups were observed or conflicting results of experiments conducted at the same conditions were reported. Thus, for example, results of various experiments on the extraction of Zr, Hf, and Rf from HF and HCl solutions^{3–6} disagreed concerning extraction sequences (see the review of Kratz⁵): Cation exchange separations (CIX) of Zr, Hf, and Rf from HF solutions, have given the following trend in ascending K_d values: $\text{Zr} > \text{Hf} > \text{Rf}$, while in the anion exchange (AIX) separations, Rf and Hf though behaving similar, were much less absorbed on the AIX than Zr.³ In contrast to results of Reference 3, recent AIX separations⁴ of group 4 elements from aqueous HCl solutions performed at the same conditions have shown an inverted sequence in rising K_d values: $\text{Rf} > \text{Zr} > \text{Hf}$. The TBP extraction of group 4 elements from 8 M HCl, however, showed the position of Rf in between those of Zr and Hf: $\text{Zr} > \text{Rf} > \text{Hf}$.⁶ Thus, extraction behavior of group 4 elements from HF and HCl solutions have not yet been established with a high certainty.

Another open question was the hydrolysis of Rf. In Reference 7, a conclusion about stronger hydrolysis of Rf in comparison with that of Zr has been drawn by studying sorption of group 4 elements and Th on cobalt ferrocyanite surfaces, while results of the AIX separations come to a different conclusion.⁸

Group 5 elements were also shown to exhibit an unexpected, inverted, trend in the complex formation and extraction from aqueous acidic HCl solutions $\text{Nb} > \text{Db} > \text{Ta}$.⁹

Solution chemistry on element 106 has shown first interesting results: In experiments on the elution of group-6 elements from cation exchange columns in 0.1 M HNO_3 , Sg was not eluted from the column in contrast to W.¹⁰ This non-tungsten-like behavior of Sg was tentatively attributed to its lower tendency to hydrolyze as compared to that of tungsten. All those open questions needed answers or theoretical interpretation.

In our previous research, numerous gas phase and aqueous phase compounds were studied theoretically. Trends in various physico-chemical properties in the transition element groups and along the last transition-element row have been defined, as well as influence of relativistic effects of those properties has

been elucidated. The reviews of those works are given in References 11, 12. To assist new experimental efforts and to solve the accumulated problems, our theoretical research has been extended to the consideration of the above mentioned processes and compounds.

In the current publication, we overview results of the recent investigations of the electronic structure and properties of gaseous species of Bh and Hs, as well as of hydrolysis and complex formation of Rf, Db, and Sg in aqueous acidic solutions along with their homologs in chemical groups.

2. Method and Details of the Calculations

Calculations of the electronic structure of the above mentioned compounds were performed using the fully relativistic Density-Functional Theory (DFT) method with the General Gradient Approximation (GGA) for the exchange-correlation energy.^{13,14} The method is a fully relativistic all-electron (or frozen core, FC, if necessary) code with the spin-orbit coupling explicitly included. It uses four-component basis functions which are transformed into molecular symmetry orbitals using double point groups. Molecular integrals between these functions are calculated in a numerical, three-dimensional grid. The most recent version of the method includes minimization of an error in the total energy¹⁵ and the integration scheme of Boerrigter et al.,¹⁶ which altogether give much more accurate results for total energies.

The Dirac Hamiltonian is

$$h_D = c\alpha\pi + (\beta - 1)c^2 + V, \quad (1)$$

where the potential is the sum of three parts

$$V = V_n + V_c + V_x, \quad (2)$$

with V_n the nuclear, V_c the Coulomb, and V_x is a functional derivative of the exchange-correlation energy. The GGA of Becke¹⁷ and Perdew¹⁸ is included perturbatively in order to consider non-local contributions. In the GGA calculations, the relativistic form of the exchange-correlation potential developed by Engel et al.¹⁹ was used.

The present calculations have been performed within the FC approximation for the group 4, 5, and 6 aqueous phase complexes and for all-electrons for group 7 and 8 gas-phase compounds. The number of integration points was 10^4 . The Mulliken population analysis²⁰ was applied for the electronic density distribution. The results were then further used for some physico-chemical models in order to link measured and calculated properties.

3. Results and their Discussion

3.1. Gas-phase Complexes

3.1.1. Group 7 Oxyhalides. Results of the RGGGA DFT cal-

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TABLE 1: Effective charges (Q_M), overlap populations (OP), ionization potentials (IP), dipole moments (μ), electric dipole polarizabilities (α), dissociation (atomization) energies (ΔH_{diss}) for MO_3Cl , where $M = \text{Tc, Re, and Bh}$.²¹

Property	TcO_3Cl	ReO_3Cl	BhO_3Cl
Q_M	1.28	1.21	1.13
OP	1.93	2.20	2.31
IP / eV	12.25	12.71	13.05
μ/D	0.93	1.29	1.95
$\alpha / 10^{-24} \text{cm}^3$	4.94	5.91	7.50
$\Delta H_{\text{diss}} / \text{eV}$	23.12	24.30 ^a	22.30

^aThermochemical ΔH_{diss} calculated via a Born-Haber cycle is 23.76 eV.

culations²¹ of the electronic structure of group 7 oxychlorides MO_3Cl ($M = \text{Tc, Re, and Bh}$) are summarized in Table 1. Typically of the transition elements in groups 4–6, the electronic structure of the Bh compound is very similar to those of Tc and Re. The values of the effective charge (Q_M) and overlap population (OP, which is a measure of covalence) show BhO_3Cl to be the most covalent compound in the row. Dipole moments and electric dipole polarizabilities of MO_3Cl increase in the group from Tc to Bh.

To predict adsorption energy, ΔH_{ads} , of BhO_3Cl on the quartz surface of the gas chromatography column, needed for the gas-phase chromatography experiments, the following model of physisorption was used. The quartz surface was supposed to be covered with adsorbed Cl. The molecule-surface interaction energy in this case was considered of consisting of three parts: molecular dipole — effective charge on Cl, molecular polarizability — effective charge on Cl and molecular polarizability — polarizability of Cl, so that

$$\begin{aligned} \varepsilon(\text{molecule-surface Cl}) &= \varepsilon(\mu, Qe) + \varepsilon(\alpha, Qe) + \varepsilon(\alpha, \alpha) \\ &= -\frac{2\mu Qe}{x^2} - \frac{Q^2 e^2 \alpha}{2x^4} - \frac{3}{2} \frac{\alpha_1 \alpha_2}{x^6 \left(\frac{1}{hv_1} + \frac{1}{hv_2} \right)}. \end{aligned} \quad (3)$$

Here, hv_1 and hv_2 denote approximately IP of the molecule and of Cl^{2-} , with the latter being a function of Q (see Reference 21). The only unknown value in eq 3 was that of x . It could be deduced, e.g. for ReO_3Cl , by setting eq 3 equal to the experimentally measured $\Delta H_{\text{ads}} = -61$ kJ/mol for a typical value of $Q(\text{Cl}) = -0.4$. This has given $x = 3.38$ Å. Taking this value as a benchmark and assuming that the molecule-surface distance was directly related to the size of the interacting molecules, $\Delta H_{\text{ads}} = -48.2$ kJ/mol for TcO_3Cl and $\Delta H_{\text{ads}} = -77.6$ kJ/mol for BhO_3Cl were determined.²¹ The increasing adsorption enthalpies (due to increasing dipole moments) mean that volatility changes in the following order: $\text{TcO}_3\text{Cl} > \text{ReO}_3\text{Cl} > \text{BhO}_3\text{Cl}$. The experimentally determined $\Delta H_{\text{ads}} = -77.8$ kJ/mol (Ref. 1) agreed very well with these predictions.

3.1.2. Group 8 Tetroxides. In a similar way, volatility of MO_4 ($M = \text{Ru, Os, and Hs}$) was predicted in Reference 22. For that purpose, the RGGA DFT fully relativistic calculations have been performed for those molecules. Results of the calculations are summarized in Table 2. As in the case of group 7 oxychlorides, HsO_4 was found to exhibit properties very similar to those of OsO_4 , and it is the most covalent and stable compound in the group, as the binding energies (ΔH_{diss}) show. The Q_M and OP data are indicative of an increase in covalence from RuO_4 to HsO_4 . Such an increase is typical of various other compounds of the transactinides and is accounted for by strong relativistic stabilization of the $7s$ and $7p_{1/2}$ valence orbitals. The calculated IPs show very good agreement with the experiment for RuO_4 and OsO_4 (Table 2). The calculated polarizabilities show a “zig-zag” behavior in the group, with the lowest value for OsO_4 .

Predictions of adsorption enthalpies of MO_4 ($M = \text{Ru, Os, and Hs}$) were made in a similar manner as those for the group 7 oxychlorides. For that purpose, a molecule-slab interaction model

TABLE 2: Effective charges (Q_M), overlap populations (OP), ionization potentials (IP), and dissociation energies (ΔH_{diss}) for MO_4 , where $M = \text{Ru, Os, and Hs}$.²²

Property	RuO_4	OsO_4	HsO_4
Q_M	1.45	1.46	1.39
OP	1.92	1.94	2.17
IP / eV (calc)	12.25	12.35	12.28
IP / eV (exp) ^a	12.19	12.35	
$\alpha / 10^{-24} \text{cm}^3$	6.48	5.96	6.26
$\Delta H_{\text{diss}} / \text{eV}$	27.48	27.71	28.44

^aReference 23.

was used where the interaction energy was integrated over the volume of a solid. The molecule - quartz surface interaction energy was considered to be of a pure van der Waals type described by the following expression²²

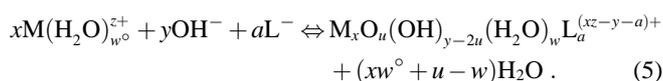
$$E(x) = -\frac{3}{16} \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right) \frac{\alpha_{\text{mol}}}{\left(\frac{1}{hv_{\text{slab}}} + \frac{1}{hv_{\text{mol}}} \right) x^3} \quad (4)$$

where $\varepsilon = 3.81$ is the dielectric constant of quartz. The interaction distance x was defined for OsO_4 in a similar way as it was done for ReO_3Cl . Using experimental values of α and IP (Table 2) for OsO_4 and setting eq 4 equal to -38 kJ/mol, $x(\text{OsO}_4) = 2.25$ Å was deduced. Then, taking this distance as a benchmark and assuming that the molecule-surface distance is directly related to the size of the adsorbed molecules, $\Delta H_{\text{ads}} = -40.4$ kJ/mol for RuO_4 and $\Delta H_{\text{ads}} = -36.3$ kJ/mol for HsO_4 were obtained.

Several other types of interaction of the molecules with the surface, like interaction with adsorbed oxygen on the surface, were also considered. In summary, $\Delta H_{\text{ads}} = -40.4 \pm 1.5$ kJ/mol and -36.7 ± 1.5 kJ/mol, on the average, have been predicted for RuO_4 and HsO_4 , respectively. Thus, HsO_4 was expected to be almost equally or slightly more volatile than OsO_4 , with the difference in the adsorption enthalpy being of the order of the experimental uncertainty. This conclusion would also be in agreement with the higher covalence of HsO_4 as compared to those of the lighter homologs.

3.2. Hydrolysis and Complex Formation of Group 4–6 Elements. In HF and HCl solutions, group 4–6 elements form mostly anionic complexes in various degree of hydrolysis. Differences in hydrolysis of compounds of elements belonging to the same chemical group are reflected by differences in their K_d (distribution coefficient) values, since more hydrolysed complexes are worse extracted than less hydrolysed ones. In the following section, a model is described which defines stability of complexes being in equilibrium with their hydrolysis products. Using this model, trends in K_d were predicted for group 4, 5, and 6 elements for ion exchange separations from aqueous acidic solutions.

3.2.1. The Model. Reactions of complex formation in equilibrium with hydrolysis are expressed in a general form by the following equilibrium



To calculate free energy of such a reaction in an efficient way, the following procedure was proposed.²⁴ The free energy of a compound was supposed to be decomposed into the following parts²⁵

$$-\Delta G^f(u, v, w)/2.3RT = \sum a_i + \sum a_{ij} - \log(u!v!w!2^w) + (2u + v + 1) \log 55.5 \quad (6)$$

and for a reaction

$$\log K = -\Delta G^r/2.3RT, \quad (7)$$

TABLE 3: Coulomb parts of the Gibbs free energies (E^C) and their changes (ΔE^C) for the reaction $M(\text{H}_2\text{O})_8^{4+} \rightleftharpoons \text{MF}_6^{2-}$ and $M(\text{H}_2\text{O})_8^{4+} \rightleftharpoons \text{MCl}_6^{2-}$, where $M = \text{Zr, Hf, and Rf}$.²⁹

Energy / eV	Compound	Zr	Hf	Rf
E^C	$M(\text{H}_2\text{O})_8^{4+}$	-53.34	-52.07	-50.92
E^C	MF_6^{2-}	-2.60	-1.18	0.23
E^C	MCl_6^{2-}	-1.21	0.41	2.13
ΔE^C	$M(\text{H}_2\text{O})_8^{4+} \rightleftharpoons \text{MF}_6^{2-}$	50.75	50.88	51.15
ΔE^C	$M(\text{H}_2\text{O})_8^{4+} \rightleftharpoons \text{MCl}_6^{2-}$	52.15	52.50	53.06

where ΔG^r is the difference in ΔG^f between products and starters of the reaction. The first term on the right-hand side of eq 6, $\sum a_i$, is the non-electrostatic contribution from all the constituent atoms, $\sum a_i = k$ OP. The next term, $\sum a_{ij}$, is a sum of each pairwise electrostatic (Coulomb) interaction:

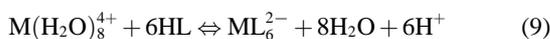
$$E^C = \sum a_{ij} = -B \sum_{ij} Q_i Q_j / d_{ij} \quad (8)$$

where d_{ij} is the distance between moieties i and j ; Q_i and Q_j are their effective charges and $B = 2.3RTe^2/\epsilon$ is an independent constant. The last two terms in eq 6 are statistical: one is a correction for indistinguishable configurations of the species, and the other is a conversion to the molar scale of concentration for the entropy.

It was further suggested²⁴ to calculate $\sum a_{ij}$ and $\sum a_i$ for each compound via the electronic density distribution data (the Mulliken numbers) obtained as a result of the fully relativistic DFT calculations of the electronic structure of the complexes of interest. The differences in those values for the left and the right parts of an equilibrium reaction plus the differences in the other terms of eq 6 define $\log K$. For that purpose, calculations of the electronic structure of numerous complexes of group 4–6 elements have been performed and free energies of the complex formation or hydrolysis reactions were defined.^{24,26–28} The results will be shown in the following subsections.

In all cases, the results have shown the hydrolysis/protonation or complex formation processes to be governed by changes in the electrostatic interaction, ΔE^C , so that prediction of an equilibrium can be made with sufficient accuracy just by calculating electrostatic terms only. This electrostatic interaction should, however, be defined using calculated relativistic electronic density distribution data and not formal charges. Thus, knowing only ΔE^C , $\log K$ could be defined for any reaction, as it is shown in the following sections for group 4, 5, and 6 complexes.

3.2.2. Complex Formation of Group 4 Elements in HF and HCl Solutions. In mixed solutions at HF between 10^{-3} M and 10^{-2} M and 0.1 M HNO_3 , i.e. at $\text{pH} \cong 1$, the complex formation for group 4 elements can be described by the following equilibrium



where $M = \text{Zr, Hf, and Rf}$, and $L = \text{F or Cl}$. To predict $\log K$ of reaction 9, the DFT calculations of the electronic structure were performed for the $M(\text{H}_2\text{O})_8^{4+}$, MF_6^{2-} , and MCl_6^{2-} complexes, where $M = \text{Zr, Hf, and Rf}$.²⁹ Geometry and bond lengths (R_e) of $M(\text{H}_2\text{O})_8^{4+}$ (D_{2d} -symmetry) and MF_6^{2-} were selected on the basis of analysis of the structural data for Zr and Hf and from calculated R_e for some simpler Rf gas-phase compounds.³⁰

The calculated electronic structure data show that the Rf complexes are very similar to those of Zr and Hf: ΔE^C for reaction 9 (Table 3) indicate that Rf should form complexes in a similar way as Zr and Hf, only at slightly higher HF concentrations. The sequence in the complex formation was, therefore, predicted as $\text{Zr} > \text{Hf} > \text{Rf}$, with the differences in the K_d values between the three elements being very small.

The theoretically obtained sequence for Zr, Hf, and Rf proved to be in agreement with the experimental sequence for descending K_d values in the sorption by CIX and for ascending K_d values for Zr and Hf in the sorption by AIX.³ The low sorption of

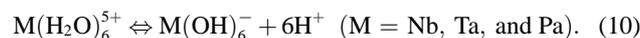
TABLE 4: Energies of E^C and ΔE^C for the hydrolysis reaction $M(\text{H}_2\text{O})_6^{5+} \rightleftharpoons M(\text{OH})_6^-$, where $M = \text{Nb, Ta, Db, and Pa}$.²⁴

Energy / eV	Compound	Nb	Ta	Db	Pa
E^C	$M(\text{OH})_6^-$	-21.74	-23.33	-21.48	-19.53
	$M(\text{H}_2\text{O})_6^{5+}$	-21.92	-25.38	-25.37	-29.71
ΔE^C		0.18	2.05	3.89	9.18

Rf at the AIX found in the experiments³ could be explained by a stronger competition of the counter ion NO_3^- for the binding sites of the resin.

In HCl solutions, at the HCl concentrations above 6 M, complex formation should follow the same pattern as that for the HF solutions (no hydrolysis takes place). Results of the theoretical treatment of equilibrium 9 with the formation of the chlorocomplexes are summarized in Table 3. The calculated ΔE^C indicate the same sequence in the complex formation, $\text{Zr} > \text{Hf} > \text{Rf}$, for HCl solutions, as that for HF solutions.

3.2.3. Hydrolysis and Complex Formation of Group 5 Elements. As a cation, Nb is known to be stronger hydrolyzed as Ta, though for the compounds of Nb and Ta the opposite trend is observed.²⁵ The hydrolysis reaction (also for Pa) proceeds very fast with the formation of the utmost hydrolysis product $M(\text{OH})_6^-$:



To study hydrolysis of Db in comparison with that of the lighter homologs in the group, the free energy changes of reaction 10 were determined for Nb, Ta, Db, and Pa on the basis of the calculations of the electronic structure of the indicated complexes using the DFT method.²⁶ Geometry and bond lengths for the Nb, Ta, and Pa complexes were taken from experimental values on the basis of analysis of the numerous structural data. The bond lengths for the Db complexes were estimated from the calculated ionic radii.³¹

The results of the calculations are shown in Table 4. One can see that E^C for $M(\text{OH})_6^-$ and $M(\text{H}_2\text{O})_6^{5+}$, where $M = \text{Nb, Ta, and Db}$, are rather similar, while those of Pa are different: E^C (absolute value) of $\text{Pa}(\text{OH})_6^-$ is lower than those of Nb, Ta, and Db, while E^C of $\text{Pa}(\text{H}_2\text{O})_6^{5+}$ is much higher. Obviously, Pa holds water molecules stronger than Nb, Ta, and Db. The differences, ΔE^C , also show strong resistance of Pa against hydrolysis, so that the trend for hydrolysis of group 5 elements is:

$$\text{Nb} > \text{Ta} > \text{Db} \gg \text{Pa}. \quad (11)$$

Thus, in agreement with experiment²⁵ Nb is confirmed to be more hydrolyzed than Ta, and both of them to be much more hydrolysed than Pa. Db is less hydrolyzed than Nb and Ta, but much more than Pa.

The formation of fluoride, chloride, and bromide complexes of group 5 elements undergoes the following complexation reaction



where $L = \text{F, Cl, and Br}$. As in the previous cases, calculations of the electronic structures of all various complexes of the group 5 elements have been performed using the DFT method and ΔE^C were defined on their basis (Table 5).^{26,27} The ΔE^C data show the following trend for formation of all the types of complexes:

$$\Delta E^C: \quad \text{Pa} \gg \text{Nb} > \text{Db} > \text{Ta}. \quad (13)$$

Thus, the theoretically obtained data show that, for all the types of complexes, those of Pa are formed in more dilute HCl solutions (starting with $\text{Pa}(\text{OH})_2\text{Cl}_4^-$ at 2–4 M), than those of Nb. The complexes of Nb start to form next, while those of Ta are formed at the highest HCl molarities. Db was shown to form

TABLE 5: ΔE^C (in eV) for reaction $M(OH)_6^- \rightleftharpoons M(OH)_n Cl_m^-$, where $M = Nb, Ta, Db, \text{ and } Pa$.²⁶

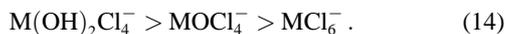
Metal	$M(OH)_2 Cl_4^-$	$MOCl_4^-$	MCl_6^-
Nb	13.56	18.40	19.57
Ta	14.32	19.80	20.78
Db	14.29	19.67	20.46
Pa	11.68	16.29	17.67

TABLE 6: ΔE^C (in eV) for reaction $M(OH)_6^- \rightleftharpoons ML_6^-$, where $M = Nb, Ta, Db, \text{ and } Pa$, and $L = F, Cl, \text{ and } Br$.^{26,27}

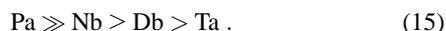
Complex	F	Cl	Br
NbL_6^-	12.20	19.57	21.40
TaL_6^-	12.69	20.78	22.63
DbL_6^-	12.38	20.46	22.11
PaL_6^-	12.19	17.67	19.91

complexes between those of Nb and Ta. This theoretical conclusion (sequence 13) for Nb and Ta (sequence 12) is in agreement with the electrodialysis experiments.³²

Comparison of the ΔE^C values for $M(OH)_2 Cl_4^-$, $MOCl_4^-$, and MCl_6^- (Table 5) shows that in agreement with the experiment, the $M(OH)_2 Cl_4^-$ species are formed at lower HCl concentration, while MCl_6^- at the highest concentrations, so that with increasing HCl concentration the complex formation changes in the order



The theoretical analysis²⁶ of the extraction mechanism of Nb, Ta, and Pa from aqueous HCl solution by anion exchange has shown that the extraction sequence is determined by the complex formation and partition of complexes between organic and aqueous phases. Taking this into account, an extraction position of Db from aqueous solutions above 4 M HCl was predicted as²⁶

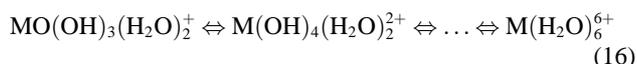
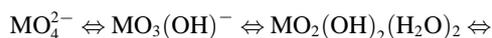


The theoretically predicted trend 15 was confirmed by the experiment on the extraction of Db and other group 5 homologs from HCl solutions.⁹ Thus, trends in the complex formation and extraction known for Nb, Ta, and Pa turned out to be inversed in going to Db. This could not be predicted by any extrapolation of properties within the group, but came out as a result of considering real chemical equilibria and calculating relativistically the electronic structure of the complexes.

The calculations have also well reproduced the sequence in the formation of ML_6^- ($M = Nb, Ta, Db, \text{ and } Pa$; $L = F, Cl, \text{ and } Br$) as a function of the ligand L, $MF_6^- \gg MCl_6^- > MBr_6^-$, as the data of Table 6 show.

3.2.4. Hydrolysis of Group 6 Elements. In HNO_3 solutions, group 6 elements form oxocomplexes with a various degree of hydrolysis. Mo is known to be more hydrolyzed than W.²⁵ The question about hydrolysis of Sg was open.

To study hydrolysis of group 6 elements, the following protonation equilibria (well-established for Mo³³) have been considered²⁸



where $M = Mo, W, \text{ and } Sg$. For that purpose, the electronic structure calculations of all the molecular species indicated in the equilibria 16 were performed²⁸ using the DFT method. Geometry and bond lengths of the Mo and W complexes were taken from experimental values by analyzing numerous structural data.³⁴⁻³⁶ The bond lengths for the Sg complexes were estimated on the basis of R_e for some simpler Sg gas-phase compounds.³⁷ The calculations were, as previously, restricted to the calculations of the ionic (Coulomb) and covalent parts of the molecular-ligand interaction energy using Mulliken numbers.

TABLE 7: Coulomb parts of the free energy changes (ΔE^C) for the step-wise protonation of MO_4^{2-} , where $M = Mo, W, \text{ and } Sg$.²⁸

Reaction	$\Delta E^C / \text{eV}$		
	Mo	W	Sg
$MO_4^{2-} + H^+ \rightleftharpoons MO_3(OH)^-$	-12.98	-13.13	-12.95
$MO_3(OH)^- + H^+ + 2H_2O$ $\rightleftharpoons MO_2(OH)_2(H_2O)_2 + H^+$	-21.43	-22.08	-21.61
$MO_2(OH)_2(H_2O)_2 + H^+$ $\rightleftharpoons MO(OH)_3(H_2O)_2^+$	-5.84	-6.35	-6.65
$MO(OH)_3(H_2O)_2^+ + H^+$ $\rightleftharpoons M(OH)_4(H_2O)_2^{2+}$	-0.43	-0.76	-1.23
$M(OH)_4(H_2O)_2^{2+} + 4H^+$ $\rightleftharpoons \dots M(H_2O)_6^{6+}$	41.97	38.71	37.11

Results of the calculations of ΔE^C for the step-wise protonation process 16 are given in Table 7. Comparing the ΔE^C data of Table 7 for negative complexes of Mo, W, and Sg one can see an extremum on W for the first two protonation steps: the largest negative values of ΔE^C for W mean its strongest preference for protonation, or the weakest preference for hydrolysis, which is in agreement with the experiments for Mo and W.²⁵ Thus, for the first two protonation steps involving the negative complexes of the elements, which are more covalent in comparison with the neutral and positively charged ones, the trend is reversed: $W > Sg > Mo$. For the further protonation processes with the formation of the positively charged complexes, ΔE^C becomes smoothly more negative from Mo to W and to Sg, so that the trend in the protonation is $Sg > W > Mo$.

Hydrolysis constants for Sg were then defined using the established relation between ΔE^C and $\log K$

$$Mo: \log K_1 / \Delta E_1^C = 3.7 / 12.98 = 0.29,$$

$$W: \log K_1 / \Delta E_1^C = 3.8 / 13.13 = 0.29,$$

$$Mo: [\log K_1 + \log K_2] / [\Delta E_1^C + \Delta E_2^C] = 7.50 / 34.01 = 0.22,$$

$$W: [\log K_1 + \log K_2] / [\Delta E_1^C + \Delta E_2^C] = 8.1 / 35.21 = 0.23 \quad (17)$$

(The $\log K$ values are from Reference 33). Thus, by using the fact that $\log K / \Delta E^C = \text{const}$ (eqs 17) and knowing ΔE^C for the Sg reactions $\log K_1(Sg) = 3.73$ and $\log K_1 + \log K_2(Sg) = 7.5$ were defined. Other $\log K$ are given in Reference 28.

Thus, the calculated ΔE^C s indicate that for the first two protonation steps involving more covalent compounds the increasing trend from Mo to W is not continued with Sg: $W > Sg > Mo$. A similar reversed trend was observed in group 5 for the formation of chloro-, bromo-, and fluoro-complexes: $Nb > Db > Ta$.^{9,24} For the further protonation processes with the formation of the positively charged complexes, ΔE^C becomes smoothly more negative from Mo to W, and to Sg, so that the trend in the protonation process is: $Sg > W > Mo$. These theoretically obtained sequences are in agreement with the experimental data on hydrolysis of Mo and W²⁵ and, recently, on Sg.¹⁰

4. Conclusions

The calculations of the electronic structures of various gas-phase and aqueous-phase compounds of the transactinides and their homologs have shown that the former are full homologs of the lighter 4d and 5d elements and exhibit very similar properties. The predicted enthalpies of adsorption of BhO_3Cl and HsO_4 indicate that trends in volatility known for the lighter compounds should be continued with the transactinides.

The study of the hydrolysis and complex formation both theoretically and experimentally has indicated that some trends could be reversed in the groups, as it was in the case of the group 5 and 6 complex formation. A careful analysis of chemical equilibria and relativistic calculations proved, therefore, to be indispensable in predictions of the outcome of liquid chromatography separation experiments.

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