Relativistic effects in physics and chemistry of element 105. III. Electronic structure of hahnium oxyhalides as analogs of group 5 elements oxyhalides

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(Received 30 January 1992; accepted 8 April 1992)

Electronic structures of MOCl₃ and MOBr₃ molecules, where M = V, Nb, Ta, Pa, and element 105, hahnium, have been calculated using the relativistic Dirac–Slater discrete-variational method. The character of bonding has been analyzed using the Mulliken population analysis of the molecular orbitals. It was shown that hahnium oxytrihalides have similar properties to oxytrihalides of Nb and Ta and that hahnium has the highest tendency to form double bond with oxygen. Some peculiarities in the electronic structure of HaOCl₃ and HaOBr₃ result from relativistic effects. Volatilities of the oxytrihalides in comparison with the corresponding pentahalides were considered using results of the present calculations. Higher ionic character and lower covalency as well as the presence of dipole moments in MOX₃ (X = Cl, Br) molecules compared to analogous MX₃ ones are the factors contributing to their lower volatilities.

I. INTRODUCTION

In the previous work we have considered electronic structure and some properties of group 5 elements pentahalides. A special attention has been given to the volatility of the pentabromides, which is a subject of intensive experimental investigations.

In macrochemistry formation of the pure pentahalides, however, is often accompanied by formation of oxyhalides. If in the case of group 4 halides it is hard to suppose the formation of MOCl₃ molecules when MCl₃ are formed, the group 5 elements are known to form easily volatile MOX₃ (X = Cl, Br) species. Thus NbOCl₃ is formed during many methods directed at the preparation of niobium pentachloride and owing to their similar volatilities they are difficult to separate (ΔH[subscript]sub] of NbCl₅ and NbOCl₃ are equal to 21.27 and 26.2 kcal/mol, respectively). In the presence of even traces of oxygen at 150–200 °C pure pentahalides transform into oxytrihalide forms. Formation enthalpies of oxytrihalides in the solid state and in the gas phase are higher than those of pure halides. Thus ΔH[subscript]form in the solid state for NbCl₅ and NbOCl₃ are 190.2 and 210.5 kcal/mol, respectively, and for the gas phase they were calculated from the Born–Haber cycle as 168.9 and 184.3 kcal/mol, respectively. (Data on the fluorides and oxyfluorides[1] nevertheless show that the former ones are more stable.) Thus the ΔH[subscript]form for TaF₅ and TaOF₅ are equal to 437.7 and 337.0 kcal/mol, respectively. MOBr₃’s are less investigated than their oxychloride analogs.

In this paper we present results of calculations of the electronic structure of the oxytrichlorides and oxytribromides of V, Nb, Ta, Pa, and of element 105, Ha, with the aim to find an analogy in their properties and, particular, in their volatilities.

In Sec. II, results of the previous experimental and theoretical investigations of the MOX₃ (M = Cl, Br) species are mentioned. Section III contains a short description of the details of the calculations in the framework of the Dirac–Slater discrete variational method (DS DVM) with self-consistent-charge (SCC) approximation. In Sec. IV results of the present molecular orbital (MO) calculations are presented. Section V is devoted to discussions of volatility of MX₃ and MOX₃ (X = Cl, Br) compounds. Conclusions are presented in Sec. VI.

II. PREVIOUS INVESTIGATIONS OF THE MOX₃ (M = V, Nb, Ta, Pa; X = Cl, Br) COMPOUNDS

A. Investigations of geometrical configurations

Of the oxyhalides MOX₃ niobium oxytrichloride is the most extensively studied. The investigations using the single-crystal x-ray diffraction technique have shown that the crystal consists of dimeric Nb₂Cl₆ units joined by niobium–oxygen linkages, so that each niobium atom has approximately octahedral coordination. The infrared spectrum confirmed the existence of bridging oxygen atoms (with a strong band at 767 cm⁻¹). Data on infrared spectroscopy show that solid NbOBr₃ contains bridging oxygen atoms like NbOCl₃. Oxytribromides are only known to follow trends noted with Nb and Ta oxytrichlorides with TaOBr₃ being much less thermally stable and disproportionating than its niobium analog.

There are very few structural gas phase data for the oxytrihalides under consideration. Electron diffraction data[7] on VOCI₃ confirm that the compound is monomeric with C₃ᵥ symmetry, the V–Cl and V–O bond lengths being 2.12 and 1.56 Å, respectively, and the CIVCl angles being
111°. The gas-phase Raman spectrum\(^7\) of NbOCl\(_3\) has shown similarity between VOCl\(_3\) and NbOCl\(_3\) with niobium-oxygen vibration at 997 cm\(^{-1}\) \((v_2)\), which was attributed to Nb==O double bond in analogy with V==O bond \((v_2 = 1035 \text{ cm}^{-1})\). On the basis of this evidence it was assumed that in the gaseous state NbOCl\(_3\) exists as a monomeric molecule possessing pyramidal \(C_3v\) symmetry.

Elements at the beginning of the actinide series have a tendency to form particularly stable MO\(^{2+}\) cations. Nevertheless, actinides form as well a variety of complexes with one metal–oxygen double bond as in complexes like [MOCl\(_3\)]\(^2-\) (M=Pa, U, Np). Oxyhalides of general formula MOCl\(_n\) in the solid state have oxygen atoms usually forming bridges. Protactinium, chemistry which sometimes resembles the chemistry of group 5 \(d\) elements, forms nonvolatile oxytrihalides. Existence of PaOCl\(_3\) has not yet been confirmed, but PaOBr\(_3\) is well investigated. PaOBr\(_3\) crystallizes with a structure which comprises chains of seven coordinated Pa atoms linked by bridging oxygen atom and bridging bromine atom: \(R(\text{Pa–O})=2.06-2.25\ \text{Å}, R(\text{Pa–Br})=2.76-3.02\ \text{Å}, R(\text{Pa–Br})=2.56-2.69\ \text{Å}\) (Ref. 8).

\(\text{Pa–O}\) stretching vibrations are observed only below 600 cm\(^{-1}\) which confirm the existence of bridging oxygen atoms. Oxyhalides of Pa are thermally unstable, but formation enthalpies can be only guessed by analogy with known values for UOCl\(_3\) and UOBr\(_3\) equal to 284.2 and 236.0 kcal/mol, respectively.\(^8\)

### B. Investigations of the electronic structures

The ability of metals to form oxyxidations MO\(^{2+}\) and complexes containing these cations with multiple metal–oxygen bond is a remarkable feature of the elements at the beginning of the transition series. The electronic structure of the halogen complexes of these oxycations have been the subject of both experimental and theoretical\(^6,10\) studies. Investigations were mainly devoted to the \(d^1\) transition metal oxohalo complexes\(^10\) and interpretations of the extreme stability of VOCI\(_2\) and complexes containing it. It was shown that the vanadium atom forms \(1\sigma\) and \(2\pi\) bonds with oxygen owing to overlap of a hybrid \(3d_\sigma^2\) orbital and \(3d_\pi^2\) ones with \(2p\)-oxygen orbitals, respectively. Molecular orbital calculations\(^10\) using the multiple-scattering \(X_\alpha\) method of the series of the \(d^1\) complexes with V, Nb, Cr, Mo, W have shown that all these complexes have basically similar electronic structures with one MO (of \(a_1\) symmetry) responsible for \(\sigma\) bonding and two MO's (of \(e\) symmetry)—for \(\pi\) bonding with oxygen. This multiple bonding is much stronger than single bonding metal–halogen. The reason is that two \(2p\), orbitals of one oxygen atom can satisfy the \(\pi\)-bonding capacities of the two \(3d\) orbitals of a transition metal. It was also shown that the strength of the metal–oxygen \(\pi\) bonding is sensitive to the nature of the ligand atoms.

### III. METHOD AND COMPUTATIONAL DETAILS OF THE MOLECULAR CALCULATIONS

#### A. SCC-DS DV method

The fully relativistic Dirac–Slater discrete variational method (DS DVM) with self-consistent charge (SCC) approximation developed by Rosen and Ellis\(^11\) has been used for the present calculations. Description of the method is given in Ref. 1. The calculations have been done both within the all-electron and the frozen core approximations and for the extended basis set including valence np\(_{1/2}\) and np\(_{3/2}\) orbitals. Results on the charge density distribution presented in the paper are for the neutral basis set. The results obtained using the ionized basis set show the same trends for the series of molecules under consideration. Numerical integration was done using 9000 integration points.

Analysis of the charge density distribution has been done using the Mulliken breakdown scheme (see Ref. 1).

#### B. Input geometrical parameters

The geometry of MOCl\(_3\) and MOBr\(_3\) (M= Nb, Ta, Ha, and Pa) by analogy with VOCI\(_3\) and NbOCl\(_3\) was assumed to be \(C_3v\). The molecules have a trigonal pyramid form with central atom above the equatorial plane and an oxygen atom above the metal. Experimental bond distances\(^3\) and angles were used for VOCl\(_3\) while for other molecules they were estimated based on the solid state structural data\(^3,14\) and differences in ionic (covalent) radii.\(^12\) Because we are not able to calculate optimal geometries we have been varying interatomic distances in quite a wide range. The influence of the specific geometry on the electronic structure will be shown in Sec. IV.

The most characteristic bond distances and angles used in the calculations are listed in Table I. The first set (a) are the shorter bond distances which were evaluated from the differences in ionic (covalent) radii\(^12\) for V, Nb, Ta, Pa, and Ha from the multiconfiguration Dirac–Fock (MCDF) calculations.\(^13\) Values (Ha\(^a\)) for HaOCl\(_3\) were assumed taking into account the relativistic bond contraction (see Ref. 1). The second set (b) are bond distances where Nb==O bond length was taken from solid state data\(^4\) for [NbOCl\(_3\)]\(^-\). The third set (c) of parameters is

### Table I. Input geometrical parameters: bond distances (Å), and O–M–L angles for MOCl\(_3\) and MOBr\(_3\).

<table>
<thead>
<tr>
<th>Distance</th>
<th>(V)</th>
<th>Nb</th>
<th>Ta</th>
<th>Ha</th>
<th>Ha(^a)</th>
<th>Pa(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) M==O</td>
<td>1.56</td>
<td>1.66</td>
<td>1.67</td>
<td>1.74</td>
<td>1.72</td>
<td>1.74</td>
</tr>
<tr>
<td>M–Cl</td>
<td>2.12</td>
<td>2.24</td>
<td>2.25</td>
<td>2.33</td>
<td>2.30</td>
<td>2.52</td>
</tr>
<tr>
<td>M==O</td>
<td>1.56</td>
<td>1.70</td>
<td>1.71</td>
<td>1.79</td>
<td>1.75</td>
<td>1.74</td>
</tr>
<tr>
<td>M–Cl</td>
<td>2.12</td>
<td>2.24</td>
<td>2.25</td>
<td>2.33</td>
<td>2.30</td>
<td>2.52</td>
</tr>
<tr>
<td>M==O</td>
<td>1.56</td>
<td>1.70</td>
<td>1.71</td>
<td>1.79</td>
<td>1.75</td>
<td>1.74</td>
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<td>2.20</td>
<td>2.29</td>
<td>2.37</td>
<td>2.34</td>
<td>2.52</td>
</tr>
<tr>
<td>(\angle\text{OMCl})</td>
<td>108°</td>
<td>109°</td>
<td>110°</td>
<td>111°</td>
<td>111°</td>
<td>111°</td>
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<tr>
<td>(\angle\text{OMBr})</td>
<td>109°</td>
<td>110°</td>
<td>111°</td>
<td>112°</td>
<td>112°</td>
<td>112°</td>
</tr>
</tbody>
</table>

\(^{a}\)Distances with relativistic bond contraction.

\(^{b}\)Bond lengths for PaOCl\(_3\) and PaOBr\(_3\) have not been varying.
for the M–Cl distances taken as in the corresponding pentahalides. The geometric parameters for MOBr₃ (a) were estimated using the set (a) for MOCl₃ taking into account differences in ionic radii of Cl and Br.

IV. RESULTS AND DISCUSSION

A. Relativistic molecular orbital splitting

In the nonrelativistic limit in the $C_{3v}$ symmetry group the $d$, $s$, and $p$ valent orbitals are transformed according to irreducible representations $A_1$ and $E$. The principal scheme of molecular orbital formation for MOCl₃ in the nonrelativistic limit is shown in Fig. 1. In the relativistic limit for the double point group $C_{3v}$ including time-reversal invariance, the $A_1$ and $E$ representations split into the double degenerate by spin $D_4$ representation and nondegenerate by spin $D_6$ and $D_s$ representations. Representation $A_1$ is transformed into the $D_s$ relativistic one. Representation $A_2$ which in the nonrelativistic limit is a linear combination of $p_π$ orbitals of ligands a pure nonbonding ligand orbital is transformed into $D_6$ relativistic representation. Double orbital degenerate representation $E$ is split into $D_s$, $D_6$, and $D_s$ relativistic representations.

In Ref. 15 interpretation of the charge-transfer transitions on the basis of the nonrelativistic MO presentation has been done for VOCl₃. In the present calculations the VOCl₃ was used as a test molecule. Results obtained along with the experimental data are presented in Table II. There is quite a good agreement between the calculated and experimental values with a fine structure of lines in the spectrum (of 161 cm⁻¹) being shown by the calculations as a consequence of relativistic energy level splitting.

B. Check of sensitivity of electron density distribution to changes in geometry

Since calculations of the optimal geometry is not possible due to insufficient accuracy of the numerical integration scheme, calculations of the electronic structure of NbOCl₃ have been done for a variety of interatomic metal–ligand distances, given in Table I, to trace the influence of this parameter on the electronic structure data. The resulting effective atomic charges, total and partial overlap populations as a function of the bond length for NbOCl₃ are shown in Table III.

Data in Table III show that the value of the effective charge on the metal atom is not very sensitive to the changes in the bond lengths. Thus an increase in M–Cl separation from 2.24–2.28 Å and in the M–O bond length from 1.66–1.70 Å results in a decrease in $Q$ by only 0.02. The summary effect of the increases in both M–O and M–Cl distances by 0.10 leads to a decrease in $Q$ of 0.05. The overlap population parameter is more sensitive to changes in the bond lengths. An increase in metal–oxygen bond length of 0.10 results in an increase in overlap population of 0.10 and an increase in the M–Cl distance brings an increase in overlap between these atoms of 0.13.

For comparison, the NbCl₅ molecule is also included in Table III.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Energy, cm⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1a_1^2) \rightarrow (1a_2)(5e)$</td>
<td>29 000</td>
<td>Experiment (Ref. 15)</td>
</tr>
<tr>
<td>$(1a_1^2) \rightarrow (1a_2)(6e)$</td>
<td>40 400</td>
<td>Present calculations</td>
</tr>
<tr>
<td>$(12D_s) \rightarrow (13D_s, D_6)$</td>
<td>29 276</td>
<td></td>
</tr>
<tr>
<td>$(12D_s) \rightarrow (30D_s)$</td>
<td>29 437</td>
<td></td>
</tr>
<tr>
<td>$(12D_s) \rightarrow (31D_s, D_6)$</td>
<td>40 406</td>
<td></td>
</tr>
<tr>
<td>$(12D_s) \rightarrow (14D_s, D_6)$</td>
<td>40 567</td>
<td></td>
</tr>
</tbody>
</table>

Table II. Charge-transfer electronic transitions for VOCl₃.

| Table III. Influence of interatomic bond distances on the charge density distribution data: effective charge ($Q$), total overlap population ($n$), and partial overlap populations ($n_{M-O}$ and $n_{M-Cl}$) for NbOCl₃ as an example. |
|---|---|---|---|
| Distance set | $R(M=O)$, Å | $R(M-Cl)$, Å | $Q$ | $n$ | $n_{M-O}$ | $n_{M-Cl}$ |
| a) | 1.66 | 2.24 | 0.99 | 1.70 | 0.59 | 1.11 |
| b) | 1.70 | 2.24 | 0.98 | 1.76 | 0.63 | 1.13 |
| c) | 1.70 | 2.28 | 0.97 | 1.82 | 0.62 | 1.19 |
| d) | 1.72 | 2.33 | 0.95 | 1.89 | 0.63 | 1.26 |

*For comparison, the NbCl₅ molecule is also included in Table III.*


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FIG. 1. Simplified MO scheme in the nonrelativistic limit for MOCl₃.
Considering sets of the interatomic distances (a) and (b) from Table I as the most realistic ones, analysis of the electronic structure of MOX₃ molecules will be done mainly for the sets (a), because our interest is rather in the tendencies in properties of the group 5 elements than in their absolute values.

C. Molecular eigenvalues and MO composition

For the interatomic distances mentioned above [Table I, set (a)] the energy level structure as a result of the calculations for VOCl₃, NbOCl₃, TaOCl₃, and HaOCl₃ is shown in Fig. 2(a)-2(b). Molecular orbital eigenvalues are given in Table IV. Bond orders and molecular orbital compositions for these molecules are given elsewhere.¹⁶ The ordering of energy levels is similar for NbOCl₃, TaOCl₃, and HaOCl₃ and valence orbital splitting in the Cᵥ symmetry group is preserved for all the molecules. The set of bonding MO’s in each compound ends with MO’s of 3p(Cl) type with admixture of the oxygen changing from 21% for NbOCl₃ to 30% for HaOCl₃ [see Ref. 16 and Fig. 2(b)]. In contrast to the nonrelativistic case, where the highest occupied MO (HOMO) has pure 100% 3pₓ(Cl) character by symmetry, in the relativistic limit this orbital is a mixed chlorine–oxygen one. Separated from the occupied orbitals by the energy gap ΔE are MO’s of predominantly d character with crystal-field splitting of d orbitals increasing from V to Ha oxychloride.

Nearly all the occupied MO’s of ligand type are mixed chlorine–oxygen except one orbital: 34D₄, 45D₄, and 55D₄ in NbOCl₃, TaOCl₃, and HaOCl₃, respectively. Energy levels below these MO’s are levels responsible for the metal–chlorine bonding and further down are MO’s responsible for the metal–oxygen interaction. In NbOCl₃ these are 28D₄, 12D₆, 12D₈, and 29D₄ MO’s. The 12D₄, 12D₆ MO’s are 3pₓ(Cl) orbitals with high contributions (40%) of 2pₓ/₂ orbital of oxygen and (28%) of niobium 4d₅/₂ orbital. Orbital 29D₄ is of σ type and 28D₄ is of σ and of π type. In TaOCl₃ orbitals responsible for metal–oxygen bonding are 39D₄–17D₆ MO’s and 42D₄ MO, which is above the metal–chlorine bonding MO’s. The same holds for the case of HaOCl₃ where the metal–oxygen 53D₄ MO is above the metal–chlorine bonding MO’s and the other three metal–oxygen MO’s are 51D₄–22D₄.

Complicated involvement of (n–1)d metal orbitals in bonding will be shown in Sec. IV E, when considering overlap electron population data. Valence ns metal orbitals have pronounced increase in contribution to bonding in going from Nb to Ha oxychloride (see Ref. 16). This especially influences vacant orbitals of d character with admixture of ns–AO (atomic orbital). Thus the percentage of ns(metal) orbitals in the highest antibonding D₄ MO (38D₄ and 49D₄ MO’s in NbOCl₃ and TaOCl₃, respectively) increases from 4.9 up to 41.0 from NbOCl₃ to HaOCl₃. This results in stabilization of 59D₄ MO in HaOCl₃ so that its position becomes below 27D₄ and 27D₆ orbitals [Fig. 2(b)]. Relativistic stabilization of ns–(metal) orbitals towards Ha will influence charge-transfer transition spectra in HaOCl₃.

Along with the results for the d-element oxytrichlorides electronic structure, data for PaOCl₃ are presented in Fig. 2 and in Ref. 16. The narrow energy separation between bonding and antibonding levels and a smaller crystal field splitting of 5f(Pa) AO’s in PaOCl₃ is evidence of a weaker metal–ligand bonding in the f-element compound compared to the d-element ones. Chemical bonding in
TABLE IV. Molecular orbital eigenvalues for MOCl₃.*

<table>
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<tr>
<th></th>
<th>NbCl₃</th>
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<th>HaCl₃</th>
<th>PaCl₃</th>
</tr>
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<tbody>
<tr>
<td>Orbital energy (eV)</td>
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<td>Orbital energy (eV)</td>
<td>Orbital energy (eV)</td>
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</tr>
<tr>
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<td>...</td>
<td>...</td>
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<td>...</td>
</tr>
<tr>
<td>38D₄</td>
<td>1.38</td>
<td>49D₄</td>
<td>1.30</td>
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</tr>
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<tr>
<td></td>
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</tr>
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*For the bond length [see Table I, set (a)].

PaCl₃ is realized by nearly equal participation of 5f and 6d AO's of Pa (see Ref. 16). In contrast to the d-element oxytrichlorides and PaCl₃ (see Ref. 1), the highest occupied MO in PaCl₃ has quite a pronounced contribution of the metal AO's. So 52D₄ is not a pure ligand orbital in PaCl₃ but it has 3.5% of 5f AO's of Pa which stabilizes this orbital and 3.9% of 6p₃/₂ AO which destabilizes this MO. The same situation has been observed in the uranyl compounds where the last occupied orbital has partial 5f character. As a consequence electron transitions from the occupied orbitals to the vacant 5f ones are not purely charge-transfer ones but have much lower intensity and are called uranyl-like transitions. The 21D₅~22D₅ orbitals in PaCl₃ are responsible for the metal–chlorine bonding. Below them are orbitals of the metal–oxygen bonding character (45D₄~46D₄). Energetic stabilization of the 5f orbitals and their spatial contraction make metal–ligand bonding weaker compared to the d element compounds.

D. Analysis of the atomic populations

Effective atomic charges and populations of the valence atomic orbitals for the series of the molecules under consideration are presented in Tables V and VI. As in the pentahalides of Nb, Ta, and Ha there is a slight increase in effective charges from Nb to Ta and there is a decrease in Q from Ta to Ha oxyhalide. Valence orbital occupancies in the nonrelativistic terms change smoothly from Nb to Ta and to Ha but in the opposite directions: \( q_s = q_s^{1/2} + q_p^{1/2} \) increases and \( q_d = q_d^{1/2} + q_d^{3/2} \) decreases. This opposite behavior of valence AO's is the reason for nearly equal effective charges on Nb and Ta, while the general tendency in the group is an obvious decrease in ionicity. From Table V one can also see that changes in bond lengths in MOCl₃ do not influence much the charge–density distribution data so that basic tendencies within the group can be observed without knowing optimal geometries.

Within group 5 trends in the electronic characteristics are similar both for the oxychlorides and the oxybromides with the latter compounds being less ionic. Taking into account this fact, analysis of the electronic structure will be mainly done for the MOCl₃ species.

If in the nonrelativistic limit the occupancies of the valence AO's show a smooth trend from Nb to Ta and to Ha compound, relativistic orbital populations have some extremes in going from Nb to Ha oxyhalides (Tables VI). There is relative stabilization of 6p₅/₂ AO in TaOCl₃(TaOBr₃) and relative stabilization of 4d₅/₂ AO in HaOCl₃(HaOBr₃). The general tendencies in the relativistic orbital behavior along the series of the oxyhalides are the same as in the pentahalides considered in Ref. 1.

E. Analysis of the orbital overlap and bonding

This unsmooth change in the valence orbital involvement in bonding in going from Nb to Ta and to Ha compounds results in different overlaps of these orbitals with...
TABLE V. Relativistic atomic orbital populations \((q_j)\), overlap populations \((n)\), effective atomic charges \((Q)\), and dipole moments \((\mu)\) for MOCl₃.

<table>
<thead>
<tr>
<th>AO</th>
<th>VOCl₃</th>
<th>NbOCl₃</th>
<th>TaOCl₃</th>
<th>HaOCl₃</th>
<th>PaOCl₃ (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R(=\text{M}=\text{O})), Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VOCl₃</td>
<td>1.56</td>
<td>1.66</td>
<td>1.67</td>
<td>1.74</td>
<td>1.72</td>
</tr>
<tr>
<td>NbOCl₃</td>
<td>2.12</td>
<td>2.24</td>
<td>2.25</td>
<td>2.33</td>
<td>2.30</td>
</tr>
<tr>
<td>TaOCl₃</td>
<td></td>
<td>2.12</td>
<td>1.94</td>
<td>1.79</td>
<td>1.80</td>
</tr>
<tr>
<td>HaOCl₃</td>
<td></td>
<td>2.08</td>
<td>1.94</td>
<td>1.79</td>
<td>1.80</td>
</tr>
<tr>
<td>PaOCl₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(q_{n\pi/2}\)  | 0.19  | 0.18   | 0.29   | 0.48   | 0.47         |
\(q_{np/2}\)   | 0.12  | 0.08   | 0.14   | 0.21   | 0.21         |
\(q_{p3/2}\)   | 0.23  | 0.14   | 0.18   | 0.12   | 0.12         |
\(q_{(n-1)d3/2}\) | 1.35  | 1.55   | 1.44   | 1.52   | 1.53         |
\(q_{(n-1)d5/2}\) | 1.95  | 2.08   | 1.94   | 1.79   | 1.80         |

\(n(=\text{M}=	ext{O})\)  | 0.59  | 0.63   | 0.72   | 0.79   | 0.78         |
\(n(=\text{M}-3\text{Cl})\) | 1.21  | 1.13   | 1.44   | 1.50   | 1.46         |
\(n(\text{tot})\) | 1.80  | 1.76   | 2.16   | 2.29   | 2.24         |

\(Q_M\)  | 1.17  | 0.98   | 1.02   | 0.89   | 0.90         |
\(Q_O\)  | -0.40 | -0.37  | -0.40  | -0.40  | -0.40        |
\(Q_{\text{Cl}}\) | -0.26 | -0.20  | -0.21  | -0.17  | -0.17        |
\(\mu, D\) | 0.48  | 0.91   | 0.99   | 1.27   | 1.27         |

\(\mu_\text{c, D}\) = 1.56 Å, \(\mu_\text{c, D}\) = 1.66 Å, \(\mu_\text{c, D}\) = 1.67 Å, \(\mu_\text{c, D}\) = 1.74 Å.

\(\mu_\text{c, D}\) = 1.72 Å, \(\mu_\text{c, D}\) = 1.72 Å, \(\mu_\text{c, D}\) = 1.74 Å.

\(\mu_\text{c, D}\) = 2.30 Å, \(\mu_\text{c, D}\) = 2.52 Å.

\(\mu_\text{c, D}\) = 0.47 Å, \(\mu_\text{c, D}\) = 0.16 Å.

\(\mu_\text{c, D}\) = 0.21 Å, \(\mu_\text{c, D}\) = 0.42 Å.

\(\mu_\text{c, D}\) = 1.14 Å, \(\mu_\text{c, D}\) = 0.88 Å.

\(\mu_\text{c, D}\) = 1.62 Å, \(\mu_\text{c, D}\) = 1.62 Å.

\(\mu_\text{c, D}\) = 1.06 Å, \(\mu_\text{c, D}\) = 1.06 Å.

\(\mu_\text{c, D}\) = 0.83 Å, \(\mu_\text{c, D}\) = 0.93 Å.

\(\mu_\text{c, D}\) = 0.03 Å, \(\mu_\text{c, D}\) = 0.03 Å.

\(\mu_\text{c, D}\) = 0.14 Å, \(\mu_\text{c, D}\) = 0.14 Å.

\(\mu_\text{c, D}\) = 0.02 Å, \(\mu_\text{c, D}\) = 0.02 Å.

\(\mu_\text{c, D}\) = 0.09 Å, \(\mu_\text{c, D}\) = 0.09 Å.

\(\mu_\text{c, D}\) = 0.12 Å, \(\mu_\text{c, D}\) = 0.12 Å.

\(\mu_\text{c, D}\) = 0.12 Å, \(\mu_\text{c, D}\) = 0.12 Å.

\(\mu_\text{c, D}\) = 0.02 Å, \(\mu_\text{c, D}\) = 0.02 Å.

\(\mu_\text{c, D}\) = 0.02 Å, \(\mu_\text{c, D}\) = 0.02 Å.

\(\mu_\text{c, D}\) = 0.02 Å, \(\mu_\text{c, D}\) = 0.02 Å.

\(\mu_\text{c, D}\) = 0.02 Å, \(\mu_\text{c, D}\) = 0.02 Å.

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\(\mu_\text{c, D}\) = 0.02 Å, \(\mu_\text{c, D}\) = 0.02 Å.

\(\mu_\text{c, D}\) = 0.02 Å, \(\mu_\text{c, D}\) = 0.02 Å.

\(\mu_\text{c, D}\) = 0.02 Å, \(\mu_\text{c, D}\) = 0.02 Å.

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\(\mu_\text{c, D}\) = 0.02 Å, \(\mu_\text{c, D}\) = 0.02 Å.

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\(\mu_\text{c, D}\) = 0.02 Å, \(\mu_\text{c, D}\) = 0.02 Å.

\(\mu_\text{c, D}\) = 0.02 Å, \(\mu_\text{c, D}\) = 0.02 Å.
energy due to both metal–oxygen and metal–chlorine interactions. Hahnium oxychloride has larger metal–ligand overlap than TaOCl₃. The little increase in covalency in HaOCl₃ with respect to TaOCl₃ is accompanied by lowering of ionicity so that the chemical bonding in HaOCl₃ seems to be weaker than that in TaOCl₃.

Protactinium oxytrichloride has multiple metal–oxygen bond as does MOCl₃ of the d elements but with a different character of bonding. From Table VII it is seen that d orbitals of Pa overlap to a less extent than those of the d elements. Valents 5f AO’s of protactinium make essential contribution to the metal–oxygen bonding. Contracted 5f orbitals give rather substantial interaction with oxygen (at a short distance) which is nearly of the order of interaction realized by 6d orbitals so that the overlap population 6d(Pa)–O=0.61 and 5f(Pa)–O=0.48. With the chlorines the 5f(metal) AO’s interact much weaker than 6d AO’s: overlap populations 6d(Pa)–Cl=1.16 and 5f(Pa)–Cl=0.45. Atomic 6p orbitals act in an antibonding way in PaOCl₃ giving negative overlap 6p(Pa)–O=–0.42 and 6p(Pa)Cl=–0.29. Finally both total overlap metal–oxygen in PaOCl₃ and overlap metal–chlorine are less than that in the d element oxychlorides (Table V) indicating the weaker chemical interaction in the f-element compounds.

The bonding for MOBr₃ is shown in Table VI. The trends in the series of the oxybromides are the same as in the oxychlorides with the MOBr₃ having higher covalency than MOCl₃ due to higher metal–bromine overlap than the metal–chlorine one.

F. Ionization potentials, electron affinities, and energies of electron transitions

The complicated behavior of the relativistic MO’s in the compounds under consideration gives rise to peculiarities in the energetic characteristics. In Table VIII data on ionization potentials (IP), electron affinities (EA), and energies of the first electronic charge-transfer transitions calculated via the transition-state procedure are given for some interatomic distances. These data show that ionization potentials for MOCl₃ increase slightly in going from VOCl₃ to HaOCl₃. The electron affinity reflects the changing position of the lowest unoccupied level in the series MOCl₃. As one can see from Table VIII the position of this level in MOCl₃ (as clearly seen in case of HaOCl₃) depends on the interatomic distances and mainly on the metal–chlorine distance. The composition of the lowest unoccupied MO is about 32%(Cl), 3%(O), and 65%(Ha) so that changes in the metal–chlorine distances influence stabilization–destabilization of this level. Thus in determining the electron affinity knowledge of the optimal geometry is needed. From Table VIII it is seen that the shorter the metal–chlorine separation the higher in absolute value is EA and the higher the energy of the first electron charge-transfer transition. Thus with strong relativistic contraction of bond lengths in HaOCl₃ stability of the pentavalent hahnium toward the process of reduction increases while any increase in bond lengths decreases this stability.

It is interesting to note that in the case of the pentahalides of the group 5 elements, tendency of hahnium to higher stability in the oxidation state 5+ for short distances is more pronounced than in HaOCl₃ where even at rather short bond lengths the electron affinity in HaOCl₃ is higher than that of TaOCl₃.

V. VOLATILITY OF THE MOCl₃ AND MOBr₃ COMPOUNDS

There are very few data on the melting points, boiling points, and heats of sublimation for MOCl₃ and MOBr₃ compounds. Vanadium oxychloride is known as a rather volatile compound boiling at 127.2°C. Its high volatility is a result of a monomeric structure in the solid state. Niobium oxychloride boils at a temperature close to that of niobium pentachloride which is equal to 247.4°C and it has a polymeric structure like other MOX₃ (M = Nb, Ta; X = Cl, Br) compounds.

Volatile as a temperature dependence of a vapor pressure on temperature has been studied only for NbOCl₃ and the corresponding relation has the form

$$\log P_m = -\frac{6349}{T}$$

Graphically this dependence along with the analogous ones for NbCl₃ and TaCl₃ are shown in Fig. 3. One can see that the vapor pressure of NbOCl₃ is lower than that of TaCl₃ and NbCl₃. Tantalum oxychloride is thermally unstable and decomposes via Ta₂O₅Cl at 300°C.
and MO$_3$r have shown that Ha is an analog of the nitro-
dependent what interaction is predominant—dispersion or
dispersions might be less than that between the pure pentahalides.

than that of Nb and Ta oxyhalides, assuming that

molecule (induction), and dispersion terms. The same

differences to the interaction energy may change in a different

racting to the interaction energy are needed because the possible constituents of this inter-
dipole-dipole, dipole-polarizable molecule) can act in opposite directions. In case of such a

can be realized owing to the relativistic bond contraction) HaOCl$_3$ should be nearly as stable to the process of

reduction as TaOCl$_3$. For exact calculations of the electron

energy of the first electron charge transfer transitions in MOX$_3$ the optimal geometries are needed. The chemical bonding in HaOCl$_3$ and HaOB$_3$ seems to be

weaker than that in Ta oxyhalides due to much lower ionic

higher boiling points of MOCl$_3$ molecules in comparison with those for NbOX$_3$ and

TaOX$_3$ ones calculations of the intermolecular interaction

to bonding in hahnium compounds compared to the tantalum ones.

To estimate the volatilities of HaOX$_3$ (X=Cl, Br) molecules in comparison with those for NbOX$_3$ and TaOX$_3$ ones calculations of the intermolecular interaction

are needed because the possible constituents of this inter-
dipole, dipole-polarizable molecule) can act in opposite directions. In case of such a

cancelling effect the difference in volatilities between

HaOX$_3$ and its analogs NbOX$_3$ and TaOX$_3$ could be less

than that between HaX$_3$ and its analogs NbX$_3$ and TaX$_3$.

Higher ionic character and lower covalency as well as the presence of dipole moments in MOCl$_3$ molecules compared to analogous MCl$_3$ are factors contributing to their lower

volatilities.

VI. CONCLUSIONS

Relativistic molecular orbital calculation of MOCl$_3$

and MOBr$_3$ have shown that Ha is an analog of the nio-
bium and tantalum oxyhalides with some peculiarities in the electronic structure determined by different spin-

orbital behavior within the group. In some basic properties

HaOCl$_3$ follows the trends in the group; there is steady

decrease in effective charges from V to Ha, increase in

covalent part of the binding energy (overlap population) and increase in molecular ionization potentials.

Stability of the oxidation state 5+ should also increase down the group and for short interatomic distances (which could be realized owing to the relativistic bond contraction) HaOCl$_3$ should be nearly as stable to the process of

reduction as TaOCl$_3$. For exact calculations of the electron

affinity and energies of the first electron charge transfer transitions in MOX$_3$ the optimal geometries are needed. The chemical bonding in HaOCl$_3$ and HaOB$_3$ seems to be

weaker than that in Ta oxyhalides due to much lower ionic

contribution to bonding in hahnium compounds compared to the tantalum ones.

To estimate the volatilities of HaOX$_3$ (X=Cl, Br) molecules in comparison with those for NbOX$_3$ and TaOX$_3$ ones calculations of the intermolecular interaction

are needed because the possible constituents of this inter-
dipole, dipole-polarizable molecule) can act in opposite directions. In case of such a

cancelling effect the difference in volatilities between

HaOX$_3$ and its analogs NbOX$_3$ and TaOX$_3$ could be less

than that between HaX$_3$ and its analogs NbX$_3$ and TaX$_3$.

Higher ionic character and lower covalency as well as the presence of dipole moments in MOCl$_3$ molecules compared to analogous MCl$_3$ are factors contributing to their lower

volatilities.

ACKNOWLEDGMENTS

One of us (V. Pershina) would like to thank Gesell-
schaft für Schwerionenforschung for financial support. We

are indebted to M. Schädel, H. Gäggeler, J. Kratz, and W.

Brüchle for several helpful discussions and to A. Rosen for

providing us with his version of the presently used DS DVM program.

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