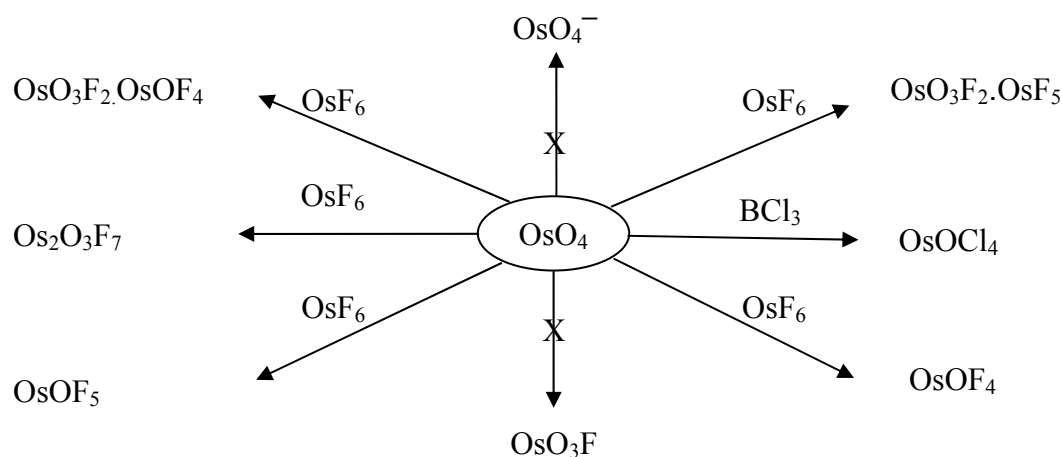


## V. Summary

The reinvestigation of osmium(VI,VII)fluoride and oxide fluoride compounds has been attempted in this work. These compounds are already reported in the literature, but are not fully characterized. The stability of the oxidation state of osmium (VII) is of particular interest.  $C_6F_6^+$  has been successfully synthesized using  $OsF_6$  as a precursor and characterized structurally as well as by ESR-spectroscopy. The fluorine containing osmium and ruthenium oxides and oxide halides are being resynthesized and investigated with single crystal X-ray determination. We hereby report the x-ray crystallographic data for these compounds. Also the structures of  $MoO_2F_2$ ,  $CrF_5$  and  $CrF_5SbF_5$  have also been determined.

In the literature there are five compounds: Os(VII)  $OsO_4^-$ ,  $OsO_3F$ ,  $OsO_2F_3$ ,  $OsOF_5$ ,  $OsF_7$ , two Osmium (VI) oxide tetrahalides  $OsOF_4$ ,  $OsOCl_4$ , and two Ruthenium(V,VI) oxide fluorides  $RuOF_3$ ,  $RuOF_4$  compounds. In this study the  $OsO_4$  is used as precursor, except for the synthesis of  $OsF_7$  and  $[OsF_7]^-$ .



### $OsO_4^-$

The synthesis of  $OsO_4^-$  as tetraphenylphosphonium tetraoxosmate has been carried out as described in the literature. However the crystal structure of the proposed compound could not be determined because of disorder of the anion in the crystal.

### $OsO_3F$

$OsO_3F$  is the first member of osmium oxide fluoride series with the highest number of oxygen

atoms. There is only one report about its possible existence. A colourless crystalline material proposed to be  $\text{OsO}_3\text{F}$  was obtained by reaction of  $\text{OsF}_6$  with glass. Through the comparison of the crystallographic data of  $\text{OsO}_4$  with the proposed  $\text{OsO}_3\text{F}$ . It could be concluded that the proposed  $\text{OsO}_3\text{F}$  is infact  $\text{OsO}_4$ .

### **$\text{OsO}_2\text{F}_3$**

It has got two modifications; one of them is a flourine-bridged polymer that was obtained by sublimation. The other is a flourine-bridged tetramer and was obtained by recrystallisation from HF. The polymer modification contains a zigzag chain of  $\text{OsO}_3\text{F}_2$  and  $\text{OsOF}_4$  units, whereas the tetramere is an eight member ring. In both compounds we found two different osmium centres. According to their oxygen and fluorine environments, one contains osmium (VI) center and the other Osmium (VIII) coexisting. The compound can be described as  $\text{OsO}_3\text{F}_2.\text{OsOF}_4$ . Since the flourine bridges are asymmetric it could be also described as  $\text{OsO}_3\text{F}^+.\text{OsOF}_5^-$ .

### **$\text{Os}_2\text{O}_3\text{F}_7$**

This new compound is green in colour. This compound has a modification similar to that of the cyclic compound  $\text{OsO}_2\text{F}_3$ . It consists of alternating  $\text{Os(V)}/\text{Os(VIII)}$  corresponding to their oxygen and fluorine environments. The entire compound can be either  $\text{OsO}_3\text{F}_2.\text{OsF}_5$  or since the flourine bridges are asymmetric, as  $\text{OsO}_3\text{F}^+.\text{OsOF}_6^-$ .

### **$\text{OsOF}_5$**

Previous reports including single-crystal structure determination have described this compound to be a monomeric species. Previously the single-crystal-structure has been calculated in space group  $\text{Pnma}$  with a two fold disorder. We have calculated our data in space group  $\text{Pna}2_1$  as a twin, resulting in better crystallographic parameters.

### **$\text{OsF}_7$**

There is also one report about the preparation of this compound. It has been synthesized by reaction of Os-metal with elemental fluorine at 600 °C and 400bar. Our product was pumped from 600°C through a 4 mm PFA tube into -196°C and the excess of  $\text{F}_2$  was pumped away

immediately. The tube was sealed off both ends. The Ramanspectrum was measured directly. Only OsF<sub>6</sub> was formed with its characteristic peak at 731 cm<sup>-1</sup>.

Other Attempts to generated OsF<sub>7</sub> failed, for example the reaction of OsF<sub>5</sub> with KrF<sub>2</sub>.

### **OsOF<sub>4</sub>**

A few methods of preparation of OsOF<sub>4</sub> are reported in the literature, but the physical data differ. We reinspected this compound and found that only the reaction of OsO<sub>4</sub> with OsF<sub>6</sub> in mol equivalents 1:3 at 180°C for many days led to the synthesis of pure dark blue OsOF<sub>4</sub>. It has got two modifications, both fluorine bridged, one is a chain polymer which was obtained through sublimation, and the other is a helical polymere which was obtained by recrystalisation from HF.

### **RuOF<sub>4</sub>**

The crystal structure of RuOF<sub>4</sub> was determined. It has been synthesized according to the literature by reaction of RuO<sub>2</sub> with diluted fluorine at 400°C in an stream system. Yellow-green crystals have been obtained. It's a fluorine bridged polymer. The speciality of this structure is the *cis* orientation of the bridging fluorine atoms with respect to the double bonded oxygen atom. This polymer is very similar to the helical structure of OsOF<sub>4</sub>.

If RuO<sub>2</sub> is treated with undiluted fluorine at 300°C, as first published in 1987, a yellow sublimate is formed. This materiel has been described as RuOF<sub>3</sub>. This compound is actually monomeric RuOF<sub>4</sub> with only very weak intermoleculer interactions. This molecule is tetragonal pyramidal with an oxygen in the apical position.

The contact to the second molecule occurs through a fluorine atom positioned *trans* to the oxygen, as expected.

### **OsOCl<sub>4</sub>**

OsOCl<sub>4</sub> has been synthesized by reaction of OsO<sub>4</sub> with excess of BCl<sub>3</sub> within one day. In the solid state it is a molecule with an almost perfect tetragonal pyramidal strukture with the oxygenatom in the apical position. Interactions to the second molecule are qualitatively similar to the molecular RuOF<sub>4</sub> monomer

**MoO<sub>2</sub>F<sub>2</sub>**

It can be obtained by pyrolysis of Na<sub>2</sub>MoO<sub>2</sub>F<sub>4</sub>. The compound exists in the solid state as cyclic trimer with three crystallographically different molybdenum atoms. The molybdenum atoms complete their octahedral coordination through contact with the lower and upper trimers with a distance of 195.2 pm.

**CrF<sub>5</sub> und CrF<sub>4</sub>SbF<sub>6</sub>**

Since chromium pentafluoride is a strong oxidizing reagent it could be able to oxidize Cl<sub>2</sub> to Cl<sub>2</sub><sup>+</sup>. However oxidation power of CrF<sub>5</sub> was not enough. Addition of a small amount of lewis acid SbF<sub>5</sub> could increase the oxidizing power of CrF<sub>5</sub>. The mixture reacts with chlorine to the well-known cation Cl<sub>3</sub><sup>+</sup> as Cl<sub>3</sub><sup>+</sup>CrF<sub>4</sub>SbF<sub>6</sub><sup>-</sup>. CrF<sub>5</sub> and CrF<sub>4</sub>SbF<sub>6</sub> were structurally characterized in the solid state they are as zigzag chain polymers. The chain of CrF<sub>5</sub> consists of octahedral CrF<sub>6</sub> units that are cis-fluorine bridged. The structure of CrF<sub>5</sub>SbF<sub>5</sub> is again that of a fluorine bridged chain but with alternating CrF<sub>6</sub> und.SbF<sub>6</sub> units.

**Cl<sub>3</sub><sup>+</sup>·OsF<sub>6</sub>As<sub>2</sub>F<sub>11</sub><sup>-</sup>**

An attempt was made to oxidize Cl<sub>2</sub> with OsF<sub>6</sub>. The oxidation power of OsF<sub>6</sub> was not strong enough. By the addition of one equivalent of AsF<sub>5</sub> the oxidation power of OsF<sub>6</sub> was increased. And lead to Cl<sub>3</sub><sup>+</sup>OsF<sub>6</sub>As<sub>2</sub>F<sub>11</sub><sup>-</sup> anion.

**The Two Structure of the Hexafluorobenzene Radical Cation, C<sub>6</sub>F<sub>6</sub><sup>+</sup>.**

We have successfully elucidated the crystal structure of C<sub>6</sub>F<sub>6</sub><sup>+</sup> cation. Single crystal structure investigations revealed that it exist in two structurally different rings. Both of these rings appear distorted from D<sub>6h</sub> symmetry. One is an Elongated ring, the other is compressed. Both rings have the same symmetry D<sub>2h</sub>. ESR spectroscopic investigation in SO<sub>2</sub>ClF resulted in a symmetrical septet. The knowledge of the structure was essential for the interpretation of the *Jahn-Teller* distortion of the cation.