V SUMMARY

The present doctoral thesis comprises the first preparation and structural characterization of the iso valence electronical compounds ReO_3F, TcO_3F and ReO_3Cl. The fundamental idea is the genesis of the cations ReO_3^+ and TcO_3^+ by halogenide abstraction. The predicted trigonal planar structure and the high electron affinity of these cations are of major interest in relation to noble gas complexes.

All compounds have C_{3v} symmetry in the gaseous state and have deformed tetrahedral coordination spheres.

According to the crystal structure analysis, ReO_3F forms helical chains bridged by fluorine and oxygen atoms, in which the rhenium is sixfold coordinated. The simultaneous presence of oxygen and flourine bridges makes this structure unique. The determination of the TcO_3F structure completes the pattern both for the line of fluoro-oxo-technetium(VII) complexes and for the line of MO_3F compounds of the seventh triad of the PSE. According to the crystal structure analysis, TcO_3F is a cyclic dimer bridged by fluorine and thus it represents a link between polymeric ReO_3F and monomolecular MnO_3F. The distorted octahedral surrounding of the technetium atoms is completed by inter-molecular interactions of the oxygen atoms. In contrast to that, the third compound ReO_3Cl, is monomolecular with *pseudo*-tetrahedral coordination geometry in all physical conditions.

Unfortunately, it has so far been impossible up to now to convert these highly reactive species into weakly coordinated MO_3^+ salts. The trials on halogenide substitution yielded in parts unexpected results. A reaction of ReO_3Cl with Lewis acids yielded the first trichloro-dioxo compound. According to x-ray crystallographic investigations, ReO_2Cl_3 is a cyclic dimer having two symmetrical chlorine bridges. Raman investigations and DFT calculations suggest a monomeric C_{2v} symmetrical structure of the compound in solution. The first reactions of ReO_2Cl_3 have shown that the compound can act as chloride donor and as chloride acceptor, respectively. ReO_2F_3, which is the fluorine analogue of ReO_2Cl_3, crystallizes in four different structural modifications as cyclic trimer, as cyclic tetramer and in the form of two open chained polymers. All modifications of the compound create distorted *pseudo*-octahedral coordination geometries, which have fluorine bridges with two double bound oxygen atoms in *cis* position. The gap concerning the structural characteristic of the fluoro-oxo-rhenium(VII) compounds has been filled by the crystal structure analysis of $ReOF_5$. This compound is monomolecular in all physical conditions, with distorted octahedral coordination. So far, the synthesis of $ReOCl_5$ has not been successful. The preparation and structure characterization of this compound still remains a demanding challenge for further studies of the highly valent transition metal halogen complexes.

Except for ReO_3Cl, the compounds follow the postulates of the VSEPR theory as they preferably form the *pseudo*-octahedral coordination geometry, which is expected for complexes having highly electronegative π-donor ligands. In parts this leads to the formation of unusual binding relations.