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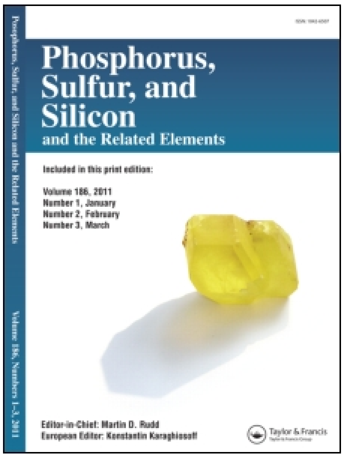

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High Coordination Among SE and TE Fluorides

Konrad Seppelt

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HIGH COORDINATION AMONG SE AND TE FLUORIDES

KONRAD SEPPELT
Institut für Anorg. und Analyt. Chemie der Freien Universität Berlin,
Fabeckstraße 34-36, D-14195 Berlin, Germany
FAX: Int. code + (30)8384289
e-mail: seppelt@chemie.fu-berlin.de

The high coordination chemistry of Te^{IV}, Se^{IV}, and Te^{VI} fluorides is reviewed, and brought into context with fluorides of neighbor elements Br, I, and Xe, but also with Mo, W, and Re fluorides. Tellurium reaches the coordination number CN 8 in case of TeF_8^{2-}. This has the same structure as IF_8^-, XeF_8^{2-}, WF_8^{2-}, ReF_8^-, and ReF_8^{2-}, namely square antiprismatic. TeF_7^- is built like a pentagonal bipyramid. It is to be compared with IF_7, IOF_6^-, XeF_7^-, WF_7^-, MoF_7^- and ReF_7. Substitution gives $CH_3OTeF_6^-$ and $(CH_3O)_2TeF_5^-$, also pentagonal bipyramidal. The highest coordination obtained for selenium fluorides may be regarded as CN 7 in SeF_6^{2-}. The slightly distorted octahedral structure is compared to BrF_6^- (octahedral) and IF_6^- and XeF_6 (strongly distorted).

Keywords: Selenium Fluorides, Tellurium Fluorides, Crystal Structures.

I. INTRODUCTION

SeF_4, TeF_4, SeF_6 and TeF_6 are well known, easy to prepare, and their physical chemistry is well documented. Especially their structural behavior is well investigated. The hexafluorides SeF_6 and TeF_6, including the technically important SF_6, are prototypes for strictly octahedral molecules exhibiting very little intermolecular interactions. SeF_6 is also inert against reaction with F^- (or bases in general), and is very alike to SF_6 in this respect. TeF_6, however, is known to add F^- under formation of TeF_7^- and TeF_8^{2-}[1].

The tetrafluorides SeF_4 and TeF_4 have certainly an SF_4 like structure in the gas phase, with two different pairs of fluorine atoms. This prevails in the structure of dissolved SeF_4 at very low temperatures[2,3]. The crystal structures are here of special interest, since they both show strong intermolecular interactions, thus an increase of the coordination number, see fig. 1. SeF_4 has two such

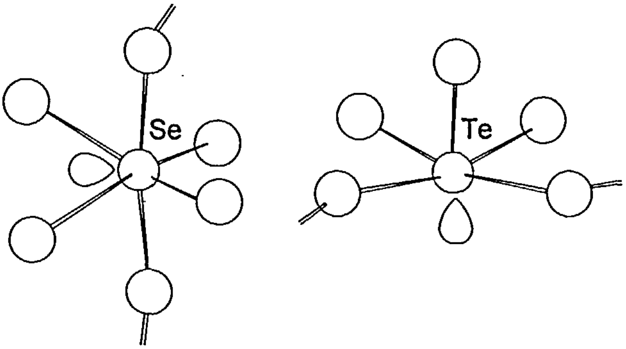

FIGURE 1 SeF_4 and TeF_4 in the solid state. SeF_4 appear as distorted octahedral, TeF_4 as square pyramidal.

contacts, the resulting coordination may be described as distorted octahedron, with only little influence of the non-bonding electron pair[4]. Nevertheless the situation may be described as a variant of

CN 7. TeF_4 has only one such intermolecular contact, the resulting geometry is square pyramidal, the sixth corner which would generate an octahedron is occupied by the non bonding electron pair, so the CN is 6[5]. These observations will play a role in the chemical behavior of SeF_4 and TeF_4 against F^-.

In a first step the anions SeF_5^- and TeF_5^- are obtained. Salts with these anions are long known[6–8].Their crystal structure show that they have the expected square pyramidal structure, with all fluorine atoms within one hemisphere around the Se and Te atom (umbrella structure). This so called IF_5 structure is conventionally discussed in terms of a strong steric influence of the non bonding electron pair.

TeF_7^- and related compounds

While the uptake of one or two F^- ions by TeF_6 has been observed a long time ago, precise information about the resulting structures was obtained only fairly recently. This is due to the effect that the F^- sources previously used have been mainly KF or CsF. The advent of pure $(CH_3)_4N^+F^-$[9] and 1,1,3,3,5,5 hexamethylpiperidium fluoride (pip^+F)[10] brought soluble and therefore recrystallisable TeF_7^- salts[11-13]. This anion has clearly a pentagonal bipyramidal structure of surprising regularity, see fig. 2.

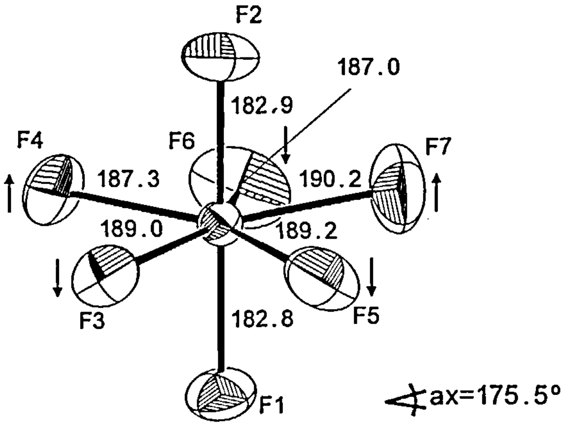

FIGURE 2 Pentagonal bipyramidal structure of the TeF_7^- anion in 1,1,3,3,5,5 hexamethylpiperidinium heptafluorotellurate VI ($pip^+TeF_7^-$). Arrows indicate deviations from the ideal plane. Distances in pm.

The two axial bonds are, as expected from simple interligand repulsion considerations, shorter than the five equatorial bonds. The only irregularity may be a non planarity of the Te atom and the five equatorial fluorine atoms (ring puckering), but these deviations are small. The TeF_7^- anion is isoelectronic to IF_7 and IOF_6^- whose structures have also recently been established as being pentagonal bipyramidal[14-19].

Reactions of CH_3OTeF_5 and trans-$(CH_3O)_2TeF_4$ with F^- afford the anions $CH_3\text{-}OTeF_6^{\ominus}$ and $CH_3O\text{-}TeF_5\text{-}OCH_3^{\ominus}$ which are also pentagonal bipyramidal with the oxygen ligands in the axial positions[20], see fig. 3.

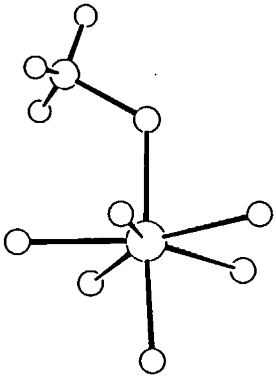

FIGURE 3 Structure of the $CH_3OTeF_6^-$ anion in $(CH_3)_4N^+CH_3OTeF_6^-$.

Reacting $OTeF_5^-$ with F^- gives $OTeF_6^{2-}$. Like with so many other salts of double charged anions, all salts of $OTeF_6^{2-}$ are very insoluble in all suitable solvents. The structure elucidation is therefore based only on vibrational data, but the outcome is clearly also pentagonal bipyramidal[21].

The CN 7 is different in so far from all smaller CN's, because there are 3 different geometry that have very similar interligand repulsion energy[22], see fig. 4, which furthermore can be interchanged by small angular variations.

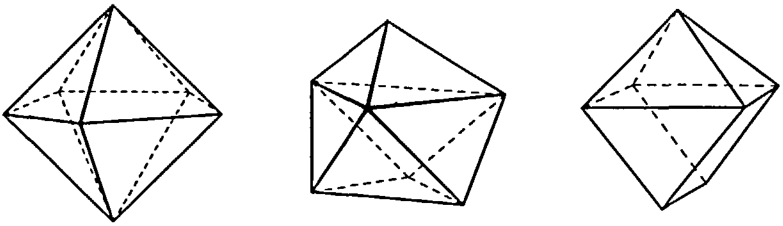

FIGURE 4 Principle geometries of the coordination number 7.

These are the pentagonal bipyramid, the capped octahedron, and the capped trigonal prism. In fact if the ligand repulsion energy would be the sole discriminating term, the capped octahedron would be most stable, followed by the capped trigonal prism. Other factors influencing the structure are, of course, special bonding situations. Even intermolecular, or in the salts regarded here, interionic interactions must be taken into consideration.

It is noteworthy that for the related anions WF_7^- and MoF_7^- the structure principle is the capped octahedron, independent of counter ion and interionic interactions[23]. It can also be shown that in TeF_7^- and its isoelectronic main group relatives the structures are independent from interionic interactions: $(CH_3)_4N^+TeF_7^-$ and $(CH_3)_4N^+MoF_7^-$ crystallize in the same space group with almost identical lattice constants, the cations being positioned identically, but the anions having a different structure. Therefore we arrive at the conclusion that a special bonding situation in TeF_7^- enforces the otherwise slightly less favorable pentagonal bipyramid. The 180° ligand - central atom - ligand situation is especially favored by the linear geometry of the bond dominating p-orbitals on Te. There are more sophisticated models to describe this situation, but they all arrive at a similar conclusion.

The influence of the electronic state is obvious from the structure of XeF_7^-[24]. Having an additional electron pair as compared to TeF_7^- the structure changes to capped octahedral, and the capping fluorine atom has a fairly long Xe-F distance, see fig. 5.

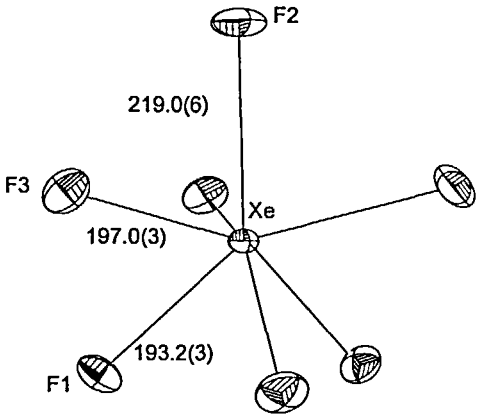

FIGURE 5 Capped octahedral structure of the XeF_7^- anion in $Cs^+XeF_7^-$.

TeF_8^{2-} and related compounds

As we will see in the following, the square (archimedean) antiprism is the structure principle of the CN 8 of all compounds here considered. Considering the ligand repulsion the trigonal dodecahedron could compete, but it is not observed. The cube, the double capped trigonal prism, and the hexagonal bipyramid have very high ligand repulsion energies and are excluded from the further discussion[22].

A square pyramid is defined by a single central atom-ligand bond distance, and one angle, e.g. the angle defined as α in fig. 6.

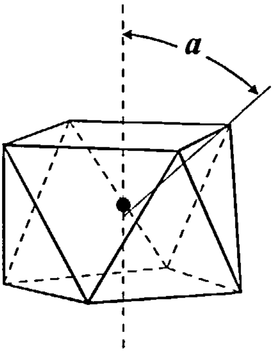

FIGURE 6 Definition of the angle α in a square (archimedean) antiprism.

In case that all adjacent interligand distances are equal (hard sphere model), which one could call an "ideal" square antiprism, α would be 59.26°. A soft sphere repulsion law with energy $\approx 1/r^6$ gives $\alpha = 57.1$[22,25].

The reaction of TeF_6 with two equivalents of CsF, first observed by Muetterties[1], has been repeated, and the resulting Cs_2TeF_8 has clearly square pyramidal structure (D_{4d}), as established by its vibrational spectra[17]. No suitable solvent for this double charged anion has been found, so fine details of the structure remain obscure.

Since an SeF_8^{2-} or even SeF_7^- clearly does not exist, we can compare TeF_8^{2-} only to non-chalcogen compounds. The closest relative is IF_8^- [26], which has indeed an almost "ideal" square antiprismatic structure, see fig. 7. Structural data are also known for WF_8^{2-}, ReF_8^{2-}, ReF_8^-, and XeF_8^{2-}, which also are all square antiprismatic, in spite of even various different electronic states[25].

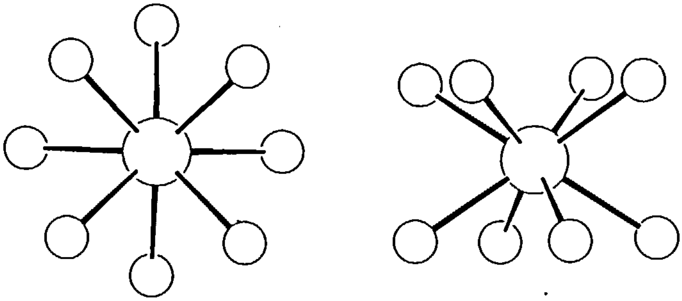

FIGURE 7 Structure of the IF_8^- in $NO^+(NOF)_2IF_8^-$, as an example for TeF_8^{2-}, which is similar, but not yet crystallographically investigated.

The case of XeF_8^{2-} is particularly telling since it is related to TeF_8^{2-} by having an additional ("non bonding") electron pair, and still has the same square antiprismatic structure. This tells us that in these highly crowded complexes the specialty of the ligand repulsion model, namely that a non bonding electron pair has a particularly large spacial demand, does not hold any longer.

The reaction product of TeF_6 with amines such as $(CH_3)_3N$ was first thought to be an eight coordinated compound, namely $[(CH_3)_3N]_2TeF_6$[27]. A careful reexamination of this reaction showed, however, that a redox reaction is taking place. Products are $[(CH_3)_3NH^+]_4\ (TeF_5^-)_3HF_2^-$ and $(CH_3)_2N\text{-}CH_2\text{-}(CH_3)_3^+\ TeF_5^-$[28].

SeF_6^{2-} and related compounds

The preparation of SF_5^-, SeF_5^-, and TeF_5^- has been described long ago[29], and their structure is fully investigated[5,6,28,30,31]. Noteworthy here may be the fact that in the salts $(CH_3)_4N^+SeF_5^-$ and $(CH_3)_4N^+TeF_5^-$ the anions behave differently with respect to interanionic interactions:[32]. While their structure is alike, the SeF_5^- anions form tetramers via Se-F...Se bridges, and the TeF_5^- form dimers, similarly via Te-F....Te bridges. The contact distances F...Se are, however, very much shorter than those between F...Te. This we take as a further indication that uptake of another F^- to SeF_5^- is more likely than in case of TeF_5^-. The first indication for this tendency was derived from the crystal structures of SeF_4 and TeF_4. And indeed, $(pip^+)_2SeF_6^{2-}$ is the only hexafluoro salt so far known in the S, Se, Te triade.

The crystal structure shows SeF_6^{2-} to be a slightly distorted octahedron[10]. Simplified the distortion can be described as a reduction from O_h to C_{3v} symmetry, with three shorter bonds that have bond angles below 90° with each other, and three longer bonds with bond angles above 90°, see fig. 8. On closer inspection one would find that there is a further reduction to C_{2v} symmetry, but the differences as compared to ideal C_{3v} are small.

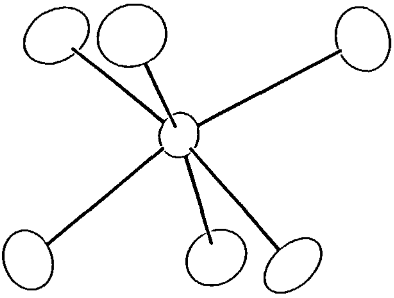

FIGURE 8 Structure of SeF_6^{2-} in a crystal of $(pip^+)_2SeF_6^{2-}$

This structure is important, since it completes the series of hexachloro, bromo, and iodo selenates and tellurates. These are ancient materials, $SeCl_6^{2-}$ was first described in 1935[33]. The structure of $TeCl_6^{2-}$ has been thoroughly investigated[34-36]. As a function of the type of cation and the lattice the $TeCl_6^{2-}$ can appear everywhere between octahedral and strongly distorted octahedral. In the octahedral cases there is good evidence for slightly non octahedral $TeCl_6^{2-}$ units being disordered, resulting in an averaged octahedral picture. IR spectra are indicative of strong, and possibly very anharmonic, deformation modes that could interchange the different distorted octahedra.

The comparison of SeF_6^{2-} with isoelectronic BrF_6^- gives an even more striking result. BrF_6^- is strictly octahedral, independent of the nature of the cations, and also according to vibrational and even n.m.r. spectroscopy [10,37]. This contrasts to the strongly C_{3v} distorted structure of IF_6^-[38], and so far it is known, to the similarly distorted structure of XeF_6[39]. The latter molecule should in the gas phase be undisturbed by intermolecular interactions. But the highly fluxional behavior of XeF_6 does not allow a precise experimental determination of the molecular structure. This is certainly one of the reasons for the vast literature on the structure of XeF_6 (which is of course not the topic of this account).

Solid and liquid XeF_6 are tetrameric and/or hexameric and cannot be used for comparison either[40–44]. Therefore we have to be content with a crystal structure in which a XeF_6 unit behaves like a solvate molecule[24]. This has a structure that can be described qualitatively similar to SeF_6^{2-}, namely a C_{3v}, or on closer inspection, even C_{2v} distorted octahedron. In contrast to SeF_6^{2-} the distortion is much stronger[24].

In order to quantify the distortion from octahedral symmetry we consider the angles formed by opposite ligands in the distorted octahedrons. Averaging these three angles implies a C_{3v} distortion, see fig. 9.

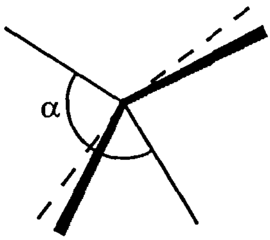

FIGURE 9 Definition of the C_{3v} distortion by the angle α of an octahedron.

The outcome is obvious: BrF_6^- 180°; SeF_6^{2-} 167°; IF_6^- 152°; XeF_6 151°.

Clearly the size of the central atoms defines the structure. Only in case of the large central atoms Xe and I there is enough space for steric activity of the nonbonding electron pair, if we want to use the nomenclature of the valence shell electron pair repulsion model. Smaller central atom sizes allow only six ligands, and the sterical crowding results in a regular octahedron as in BrF_6^-. SeF_6^{2-} is an intermediate case.

Increase of the size of the ligand should show an opposite effect: The amount of distortion form regular octahedral geometry is expected to diminish in the sequence.

$SeF_6^{2-} > SeCl_6^{2-} > SeBr_6^{2-} > SeI_6^{2-}$

$(TeF_6^{2-}) > TeCl_6^{2-} > TeBr_6^{2-} > TeI_6^{2-}$

For unknown TeF_6^{2-} a strongly distorted structure is predicted, certainly more distorted than in SeF_6^{2-}, and possibly even little more than in IF_6^- and XeF_6.

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