Stereochemistry of complex tellurium(IV) fluorides

Yu.E.Gorbunova, Yu.V.Kokunov and Yu.A.Buslaev

Kurnakov Institute of General and Inorganic Chemistry, USSR
Academy of Sciences, Leninsky pr.,31, Moscow, 117071, USSR

Abstract – The structures of about 20 tellurium (IV) fluoride
complex compounds prepared have been studied. In these
compounds lone pair (LP) of electrons is stereochemically
active and occupies one coordination position. Fluorooxohyd-
roxocomplexes containing 2–3 fluorine atoms in their inner
sphere are built of trigonal bipyramids with LP at an equato-
rial position. Tellurium oxofluorides and fluorides with the
number of fluorine atoms from 3 to 5 form pseudooctahedra.
Stereochemical activity of LP in compounds of Sn(II), Sb(III),
Te(IV), I(V) and Xe(VI) is discussed.

The structure of tellurium fluoride (IV) compounds reflects the typical
features of stereochemistry of non-transition element compounds.

The valence shell electron-pair repulsion (VSEPR) theory advanced by
Gillespie and Nyholm appeared to explain the structure of non-transition
element complexes the most successfully. The model by Randle and Masher
considers, in addition to the ordinary two-electron two-centre (CV) bonds,
the 4-electron 3-centre hypervalent bonds formed by the central atoms'
lone pair of $p\sigma^2$ electrons and two single σ-electrons of ligands (HV-1)
and hypervalent bonds due to participation of the central atoms ns^2-orbitals
(HV-2). The latter bonds cause the most symmetrical geometry of molecules
(for inst. SF_6 and IF_7). It is hardly to be emphasized that both, the VSEPR
model and the hypervalent bond theory (an approximate MO approach), are the
extreme cases possessing their own limitations.

All the approaches are at present widely used and the preference is given
to the model that describes the structure of compounds the most consistently.

The complexes of tellurium (IV) fluoride are the most stable, the lone pair
(LP) of electrons being stereochemically active and occupying one coordina-
tion position.

We have prepared and studied about 20 tellurium (IV) complex compounds.
Fluorooxohydroxocomplexes containing 2–3 fluorine atoms in their inner
sphere are built of trigonal bipyramids with a LP at an equatorial position
(Fig.1,2). The fluorine atoms located in the $Te_2O(OH)_2F_4$ at greater
distances from the Te atom than oxygens could be expected to make bridges
but the F–Te–F fragments have been found to be linear in all the compounds
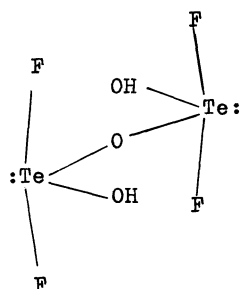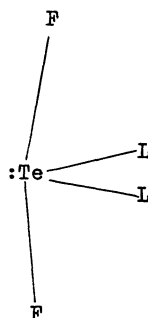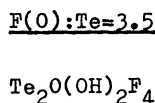including those with the ratio F(O):Te=4. (Fig.2).

F(O):Te=3.5

$Te_2O(OH)_2F_4$

F(O):Te=4

$NH_4TeO(OH)F_2$

$KTeOF_3$

$(NH_4)_2Te(OH)F_3SO_4$

$Na_2Te(OH)F_3SO_4$

$RbTeF_4NO_3$

$NH_4Te(OH)_2F_2NO_3$

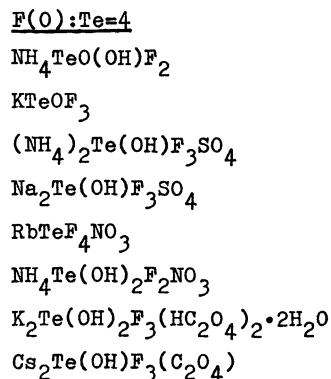$K_2Te(OH)_2F_3(HC_2O_4)_2\cdot 2H_2O$

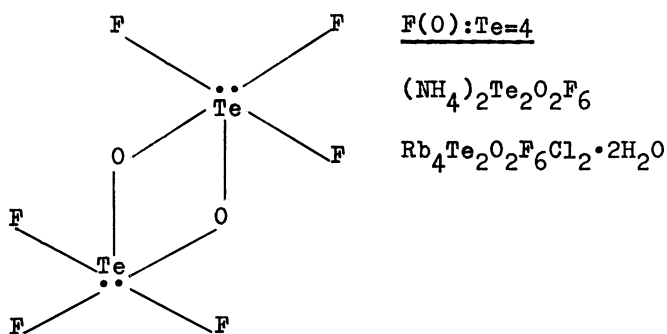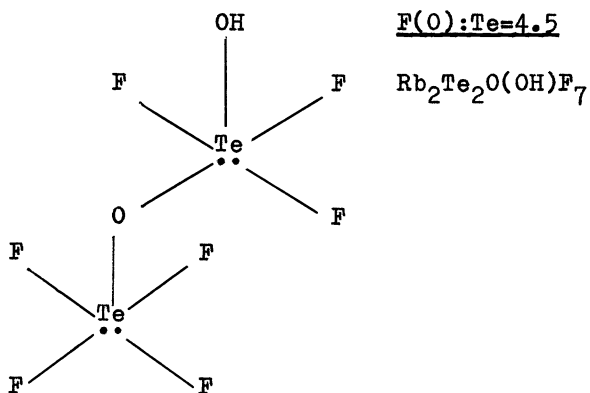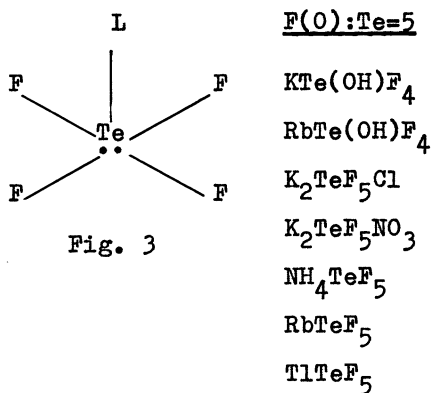$Cs_2Te(OH)F_3(C_2O_4)$

Fig. 1

Fig. 2

Tellurium oxofluorides and fluorides with the number of fluorine atoms from 3 to 5 form pseudooctahedra with the LP occupying one of the coordination positions (Fig.3,4,5). The interatomic Te-F and Te-O distances as well as stereochemical behaviour of both fluorine and oxygen ions are highly similar due possibly to accepting an electron by the oxygen atom becoming as a result isoelectronic (s^2p^5) to the F atom.

F(0):Te=5

KTe(OH)F$_4$

RbTe(OH)F$_4$

K$_2$TeF$_5$Cl

K$_2$TeF$_5$NO$_3$

NH$_4$TeF$_5$

RbTeF$_5$

TlTeF$_5$

Fig. 3

F(0):Te=4.5

Rb$_2$Te$_2$0(OH)F$_7$

Fig. 4

F(0):Te=4

(NH$_4$)$_2$Te$_2$O$_2$F$_6$

Rb$_4$Te$_2$O$_2$F$_6$Cl$_2$·2H$_2$0

Fig. 5

In the trigonal bipyramidal compounds of type TeL$_4$E the equatorial bond distances are according to the X-ray data shorter than the axial ones, the LP locating in equatorial plane.

Te - F$_{ax}$	1.93 - 2.07 Å
Te - F$_{eq}$	1.81 - 1.95 Å
Te - 0/H/$_{eq}$	1.89 - 2.02 Å
Te - O$_{eq}$	1.84 - 1.90 Å
F$_{ax}$ - Te - F$_{ax}$	154.1 - 166.9°
L$_{eq}$ - Te - L$_{eq}$	93.0 - 101.2°

The Te atom in pseudooctahedral (TeF$_5$E) compounds is displaced by 0.19 - 0.44 Å towards the LP direction, the axial bond at trans-position to the LP being shortened.

Te - L$_{ax}$	1.80 - 1.92 Å
Te - L$_{eq}$	1.91 - 2.26 Å

The shortening of axial bonds $\triangle$ D is observed throughout the whole series:

|			
$SbF_5^=$	TeF_5^-	IF_5	XeF_5^+
$\triangle$ D 0.04 - 0.16	0.09 - 0.12	0.03 - 0.12	0.01 - 0.13 (Å)
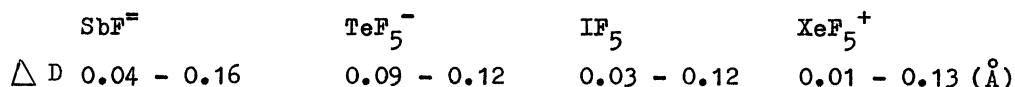
The pseudooctahedral configuration of TeF_5^- and IF_5 remains in solutions which is evidenced by the ^{19}F NMR spectrum of type AB_4.

The replacement of the F atom by different ligand (OH^- or OR^-) disturbs firstly the axial F atom.
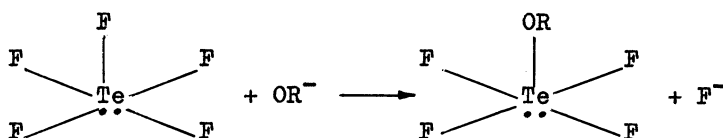

This confirms the concept that more covalently bonded ligand replaces the most strongly bonded atom.
Aminoalcohol behaves as a bidentate ligand:
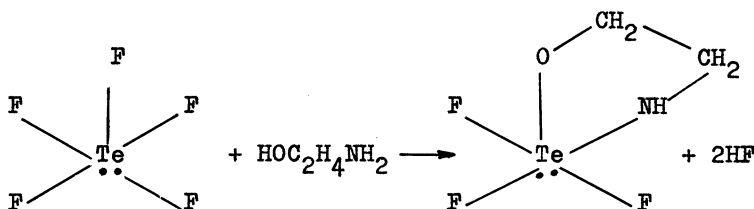
The study of the TeF_5^- and IF_5 molecules in solution suggests the AF_5 molecules to be open from the LP side so that up to 4 dipole molecules can be oriented by IF_5 at this side to compensate the positive charge on the central atom:
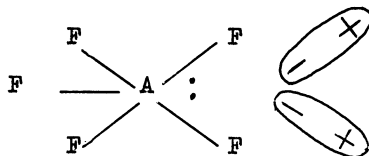
The addition (in the ratio 10:1) of amine into the IF_5 solution smears the fine structure of the NMR spectrum due to a fast exchange between the amine molecules oriented at the LP side.

As it follows from general considerations the stereochemical activity of LP decreases from right to left and down the periodic Table. This suggestion is however not easy to confirm experimentally due to a lack of data on electron distribution in the appropriate compounds so that no numerical estimation of the LP activity throughout the rows and periods has so far been made.

The increasing activity of the LP or distortion of spherical symmetry of ns^2 orbitals due to admixture of p-character repulses the bonding electron pairs hence decreasing the O - A - O angle throughout the series of pseudo-tetrahedral oxoanions:

	O_1AO_2	O_1AO_3	O_3AO_2 , °
XeO_3	103	103	103
IO_3^-	98	96	98
$TeO_3^=$	88	86	77

And throughout the series of pseudotetrahedral fluorides:

	F_1AF_2	F_1AF_3	F_2AF_3 ,°
TeF_3^+	88	86	77
SbF_3	89	84	84
SnF_3^-	83	83	83

This enables one to conclude that the stereochemical activity of the LP increases from xenon to tin

$$XeO_3 \quad IO_3^- \quad TeO_3^=$$
$$TeF_3^+ \quad SbF_3 \quad SnF_3^-$$
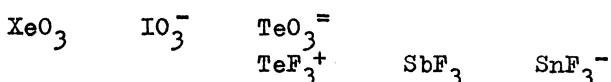
One of the interesting properties of complexes with LP is their long order interactions occuring at the side of LP location. The positively charged central nucleus is open from that side and several atoms of foreign molecules can approach here to form weak valent bonds and hence compensate positive charge on the nucleus. A sufficient volume of data is at present available to consider the details of screening various polyhedra at the side of LP location in the non-transition element complexes.

The number of atoms surrounding the LP in the crystals is different. It is maximal (4-5) for the pseudotetrahedral molecule; in trigonal bipyramids this number reduces to 3-4 atoms; in pseudooctahedra it varies as follows:

$F_5Sb^=$: distant fluorine atoms at 3.78 Å

F_5Te^- : 2-3 fluorine atoms at 3.35 Å

F_5I : 4 fluorine atoms at 3.14 Å

F_5Xe^+ : 4 fluorine atoms at 2.60 - 2.92 Å
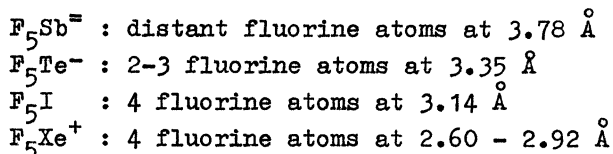
One can conclude considering the number and distances listed that, first, these non-valent interactions are electrostatic in nature and, second, with the oxidation state increasing along the series Sb(III), Te(IV), I(V), Xe(VI) the character of LP changes considerably (the electron density of S - AO increases).

In connection with the details of long order environment it is important to pay attention to the ability of antimony and tellurium fluorides to form mixed compounds containing the ions Cl^-, NO_3^-, $SO_4^=$, $C_2O_4^=$, etc. Neither of these anions can compete with fluorine for entering the first coordination sphere and localizes at the side of the LP position.

The formation by IF_5 of the complexes of composition $NaIF_5Br$, KIF_5Cl or $K_2IF_5SO_4$ might possibly be expected if appropriate solvents are found.

TABLE 1. Systematization of the types of complexes formed by non-transition element fluorides

CV	HV-1					electron configuration CV + LP	type of polyhedrum
2	SnF_2	SbF_2^+					
3	SnF_3^-	SbF_3	TeF_3^+			sp^3	ψ-tetrahedrum
2 2	$SnF_4^=$	SbF_4^-	TeF_4	IF_4^+	XeF_4^{++}	sp^2	ψ-trigonal bipyramide
1 4	$SnF_5^{\equiv}$	$SbF_5^=$	TeF_5^-	IF_5	XeF_5^+	sp	ψ-octahedrum
	6	$SbF_6^=$	$TeF_6^=$	IF_6^-	XeF_6		octahedrum
	7			$IF_7^=$	XeF_7^-		
	8				$XeF_8^=$		

The increasing number of fluorine atoms in the inner sphere is accompanied by formation of hypervalent HV-1 bonding while the complexes of composition AF_6, AF_7, AF_8 form hypervalent HV-2 bonds involving valent s^2 orbitals of the central atom so that all the bonds become equivalent and the octahedrum AF_6 becomes regular. In AF_7 and AF_8 the fluorine ions occupy the apices of regular polyhedra. The existence of stable XeF_6 and $XeF_8^=$, unstable IF_6^- and the absence of $TeF_6^=$ and $SbF_6^\equiv$ evidence for the high stereochemical activity of LP in antimony (III) and tellurium (IV) fluorides. The decomposition reaction

$$TeF_6^= \;\rightleftharpoons\; TeF_5^- + F^-$$

can be presented as:

$$6(HV\text{-}1)bonds \longrightarrow 1(CV)bond + 4(HV\text{-}1)bonds$$
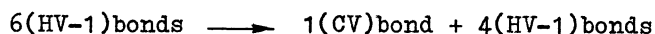
considering the change in bonding.

The solid XeF_6 is known to decompose spontaneously producing XeF_5^+ according to a similar scheme, the bridging fluorine ions F^- binding the cations into tetra- and hexamers.

The formation of cations is favoured by the increasing number of strong covalent bonds according to the scheme:

$$TeF_4 \longrightarrow TeF_3^+ + F^-$$
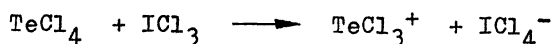$$2(CV) + 2(HV\text{-}1) + LP \longrightarrow 3(CV) + LP$$
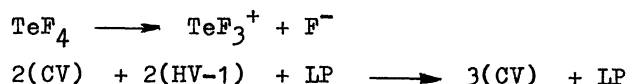
as well as by the energy gain due to electrostatic interaction of the cation with several fluorine ions.

The acid-base equilibrium reactions with transfer of chloride-ion can also be considered from the view-point of disproportionating bonds:
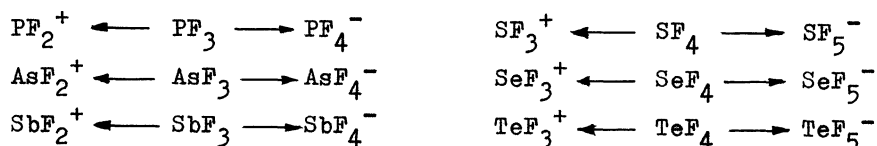
$$SCl_4 + ICl_3 \longrightarrow SCl_3^+ + ICl_4^-$$

or

$$TeCl_4 + ICl_3 \longrightarrow TeCl_3^+ + ICl_4^-$$
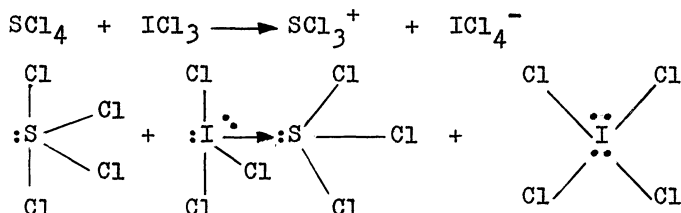
where 3CV Te_o- Cl bonds in $TeCl_3^+$(2.27Å) are 0.06 Å shorter than in the $TeCl_4$ (2.33 Å).

The formation of AF_2^+ cations is unknown since the lost of one of the three covalently bonded fluorine atoms is not favourable from the view point of energy while all the tetrafluorides AF_4 with two hypervalent bonds show the bond disproportioning:

$$PF_2^+ \longleftarrow PF_3 \longrightarrow PF_4^- \qquad SF_3^+ \longleftarrow SF_4 \longrightarrow SF_5^-$$
$$AsF_2^+ \longleftarrow AsF_3 \longrightarrow AsF_4^- \qquad SeF_3^+ \longleftarrow SeF_4 \longrightarrow SeF_5^-$$
$$SbF_2^+ \longleftarrow SbF_3 \longrightarrow SbF_4^- \qquad TeF_3^+ \longleftarrow TeF_4 \longrightarrow TeF_5^-$$

The same is observed for the chlorides: the salts with the PCl_2^+, $AsCl_2^+$ and $SbCl_2^+$ cations have not been prepared while the cations SCl_3^+, $SeCl_3^+$ and $TeCl_3^+$ are well known.

As to the complex antimony and tellurium chlorides the stability of regular octahedral hexachloroanions $SbCl_6^{\equiv}$, $TeCl_6^{=}$ attracts attention which means that the following reaction of complex formation is characteristic for the chlorides:

$$SbCl_5^{=} + Cl^{-} \longrightarrow SbCl_6^{\equiv}$$

$$TeCl_5^{-} + Cl^{-} \longrightarrow TeCl_6^{=}$$
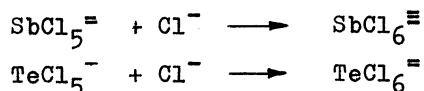
or according to the scheme of the central atom bonds' transformation:

$$1(CV) + 4(HV-1) + LP \longrightarrow 6(HV-1) + LP$$
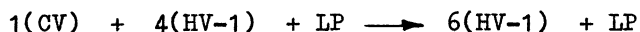
One more crystallochemical difference between the complex fluorides and chlorides consists in the following. In antimony chlorides the covalently bonded Sb(III) - Cl distances vary within 2.33 - 2.79 Å while the bridging chlorine atoms at the side of the antimony LP lie at the distances 2.81-3.62 Å (average over 57 distances is 3.18 Å) while the short and long range interatomic distances in fluorides differ much more essentially (more than 1 Å).

One can therefore suggest the addition bonding including valent, to be present in chlorides due to the lone pair of chlorine electrons. This very reason, namely considerably different nature of bonding in non-transition element chlorides and fluorides with the lone pairs of electrons seems to account for the absence of mixed halogenocompounds containing both fluorine and chlorine atoms at typical metal-ligand distances. For instance, the $Rb_2SbF_2Cl_3$ salt undergoes disproportioning in solid state to give Rb_3SbCl_6 and $Rb_3Sb_2F_6Cl_3$. At the same time mixed antimony (V) and tellurium (IV) fluorochlorides are known for a long time.

REFERENCES

1. Yu.V.Kokunov, Yu.D.Chubar, M.P.Gustjakova, Yu.A.Buslaev, Koord.Khim., USSR 6, N 12, 1838-1845 (1980).
2. Yu.E.Gorbunova, S.A.Linde, V.I.Pakhomov,Yu.V.Kokunov, M.P.Gustjakova, Yu.A.Buslaev, Koord.Khim., USSR, 8, N 3, 389-395 (1982).
3. Yu.E.Gorbunova, S.A.Linde, V.I.Pakhomov, Yu.V.Kokunov, M.P.Gustjakova, Yu.A.Buslaev, Koord.Khim.,USSR, 9, N 4, 524-535 (1983).
4. Yu.E.Gorbunova, S.A.Linde, V.I.Pakhomov, Yu.V.Kokunov, M.P.Gustjakova, Yu.A.Buslaev, Koord.Khim., USSR, 10, N 3, 340-349 (1984).
5. Yu.E.Gorbunova, S.A.Linde, V.I.Pakhomov, Yu.V.Kokunov, M.P.Gustjakova, Yu.A.Buslaev, In the book "VII All-Union Symposium on inorganic fluorides chemistry", M., Nauka, USSR, 18 (1984).
6. Yu.E.Gorbunova, S.A.Linde, V.I.Pakhomov, V.A.Sarin, N.N.Bydanov, Yu.V. Kokunov, M.P.Gustjakova, Yu.A.Buslaev, Koord.Khim.,USSR, 11, N 2, 270-276 (1985).
7. Yu.E.Gorbunova, S.A.Linde, V.I.Pakhomov, Yu.V.Kokunov, M.P.Gustjakova, Yu.A. Buslaev, Koord.Khim.,USSR, 11, N 3, 378-384 (1985).
8. Yu.E.Gorbunova, S.A.Linde, V.I.Pakhomov, Yu.V.Kokunov, M.P.Gustjakova, Yu.A.Buslaev, Koord.Chim.,USSR, 12, N 6, 835-839 (1986).