

10.3: Compounds of Chlorine

Comparison to fluorine

To appreciate the chemistry of chlorine in comparison to that of fluorine it is necessary to appreciate the differences and trends between the elements. As may be seen in Table 10.3.1, chloride is significantly larger than fluorine. In addition while chlorine is an electronegative element its electronegativity is significantly less than that of fluorine, resulting in less polar bonding.

Table 10.3.1: Comparison of physical characteristics for fluorine and chlorine.

Element	Ionic radius (Å)	Covalent radius (Å)	van der Waal radius (Å)	Electronegativity
Fluorine	1.33	0.64	1.47	-4.1
Chlorine	1.81	0.99	1.75	-2.9

The X-Cl bond is an electron pair covalent bond with a highly polar nature. In this regard, chlorine is similar to fluorine. However, there are two key features with regard to chlorine's bonding that differentiates it from fluorine.

1. Unlike fluorine, chlorine can form multiple covalent bonds, e.g., ClO_4^- and ClF_3 .
2. Unlike fluorine, chlorine can form π -bonds with oxygen, i.e., $\text{Cl}=\text{O}$.

The chloride ion (Cl^-) forms salts with ionic lattices (e.g., NaCl) but also forms a wide range of complexes, e.g., $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and $[\text{RhCl}_6]^{3-}$. Chloride also acts as a bridging ligand in which one, two or three chlorides can bridge two metal centers (Figure 10.3.1).

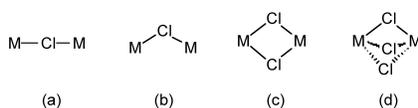


Figure 10.3.1: Structures of common halide bridging moieties.

Chloride (and bromide) bridges are usually bent, whereas fluoride bridges can be either linear or bent. As an example, BeF_2 and BeCl_2 are isostructural, consisting of infinite chains with bent bridges (Figure 10.3.2). In contrast, transition metal pentahalides show different structures depending on the identity of the halide. This, TaCl_5 dimerizes with bent bridges (Figure 10.3.3a), while TaF_5 forms a cyclic tetramer with linear fluoride bridges (Figure 10.3.3b).

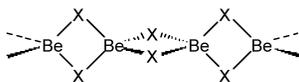


Figure 10.3.2: The solid state structure of BeX_2 ($X = \text{F}$ or Cl).

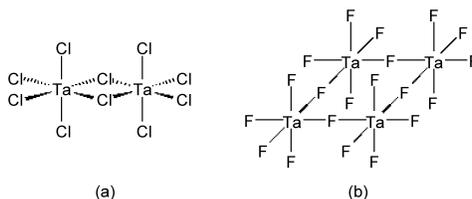


Figure 10.3.3: The solid state structure of (a) TaCl_5 and (b) TaF_5 .

The halide bridge

The bridging halide bonds can be described by both Lewis and molecular orbital (MO) theory. In a simple picture, the lone pair of a terminal halide can be thought to act as a Lewis base donor ligand to the second Lewis acidic metal center. Indeed some bridging halides are asymmetric consistent with this view; however, the symmetrical ones can be described by a resonance form. From a molecular orbital point of view, the bridging halide is represented by a combination of two metal centered orbitals with two halogen orbitals.

Hydrogen chloride

Hydrogen chloride (HCl) is prepared by the reaction of concentrated sulfuric acid (H_2SO_4) with either NaCl or concentrated HCl solution.

Hydrogen chloride is a polar molecule with a dipole of 1.08 D. However, the lower polarity as compared to that of hydrogen fluoride (1.91 D) is consistent with the physical and chemical properties. Hydrogen chloride is a gas at room temperature (Mp = -114.25 °C, Bp = -85.09 °C), and its low boiling point is consistent with weak hydrogen bonding in the liquid state. While self-ionization, (10.3.1), is very small, liquid HCl dissolves some inorganic compounds to give conducting solutions, (10.3.2).



Hydrogen chloride is soluble (and reacts) in water, (10.3.3). The pK_a of the reaction (-7.0) is larger than observed for fluorine (3.2) and as such HCl is a stronger acid than HF.



Oxides of Chlorine

Chlorine forms a series of oxides (Table 10.3.2) in which the chlorine has the formal oxidation states +1, +4, +6, and +7. The physical properties of the oxides are summarized in Table 10.3.2. While, the oxides of chlorine are not very stable (in fact several are shock sensitive and are prone to explode) the conjugate oxyacids are stable.

Table 10.3.2: Physical properties of the oxides of chlorine.

Compound	Mp (°C)	Bp (°C)
Cl_2O	-116	4
ClO_2	-5.9	10
Cl_2O_4	-117	44.5
Cl_2O_6	3.5	unstable
Cl_2O_7	-91.5	82

Dichlorine monoxide (Cl_2O , Figure 10.3.4a) is a yellowish-red gas that is prepared by the reaction of chlorine with mercury oxide, (10.3.4), or with a solution of chlorine in CCl_4 .

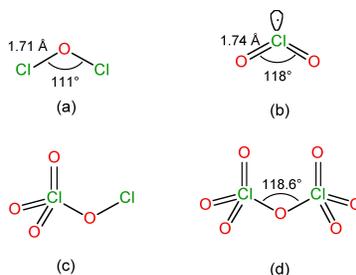


Figure 10.3.4: The structure of (a) Cl_2O , (b) ClO_2 , (c) Cl_2O_4 , and (d) Cl_2O_7 .

When heated or subject to a spark, Cl_2O explodes to Cl_2 and O_2 . Dichlorine monoxide reacts with water to form an orange-yellow solution of hypochlorous acid, (10.3.5).



Chlorine dioxide (ClO_2) is a yellowish gas at room temperature and is commonly used in industry as an oxidizing agent. The best synthesis of ClO_2 involves the reduction of potassium chlorate (KClO_3) by oxalic acid at 90 °C, since the CO_2 formed acts as a diluent for the highly explosive ClO_2 . On an industrial scale ClO_2 is made by the exothermic reaction of sodium chlorate with SO_2 in sulfuric acid, (10.3.6). The photolysis of ClO_2 yields a dark brown solid with the formula Cl_2O_3 ; however, its facile explosive decomposition precludes study.



The structure of ClO_2 (Figure 10.3.4b) is equivalent to SO_2 with one extra electron, resulting in a paramagnetic unpaired electron species. Unusually, despite the unpaired electron configuration, ClO_2 shows no tendency to dimerize. This is unlike the analogous NO_2 molecule.

Dichlorine tetraoxide (Cl_2O_4) is commonly called chlorine perchlorate as a consequence of its structure (Figure 10.3.4c). Dichlorine hexaoxide (Cl_2O_6) is an unstable red oil that has the ionic structure in the solid state: $[\text{ClO}_2]^+[\text{ClO}_4]^-$.

Dichlorine heptoxide (Cl_2O_7) is a relatively stable oil, that is prepared by the dehydration of perchloric acid at $-10\text{ }^\circ\text{C}$, (10.3.7), followed by vacuum distillation. The structure of Cl_2O_7 (Figure 10.3.4d) has been determined by gas phase electron diffraction.



The reaction of Cl_2O_7 with alcohols and amines yields alkyl perchlorates (ROClO_3) and amine perchlorates (R_2NClO_3), respectively.

Fluorides of chlorine

Given the isolobal relationship between the halogens it is not surprising that the mixed dihalogens can be prepared, e.g., ClF , ICl , and BrCl . Chlorine fluoride is a highly reactive gas (Bp = $-100.1\text{ }^\circ\text{C}$) that is a powerful fluorinating agent, and is prepared by the oxidation of chlorine by chlorine trifluoride, (10.3.8).



The higher electronegativity of fluorine as compared to chlorine (Table 10.3.1), and the ability of chlorine to form more than one bond, means that higher fluorides of chlorine are also known, i.e., ClF_3 and ClF_5 . Chlorine trifluoride (ClF_3 , Bp = $11.75\text{ }^\circ\text{C}$) is a useful fluorinating agent, that is prepared by the high temperature reaction of elemental chlorine and fluorine, is a useful fluorinating agent. The gaseous pentafluoride (ClF_5 , Bp = $-31.1\text{ }^\circ\text{C}$) is prepared by the reaction of potassium chloride with fluorine, (10.3.10).



The structure of ClF_3 is T-shaped with two lone pairs on chlorine (Figure 10.3.5a), while that of ClF_5 is square pyramidal with a single lone pair on chlorine (Figure 10.3.5b).

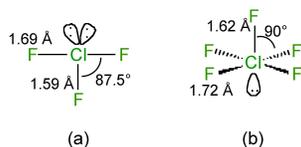
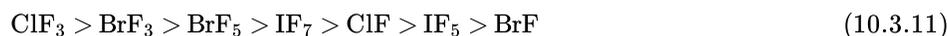
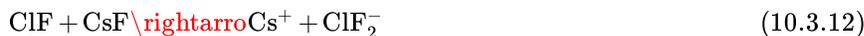


Figure 10.3.5: The structures of (a) ClF_3 and (b) ClF_5 .

In general the halogen fluorides are very reactive; explosive reactions occur with organic compounds. They are all powerful fluorinating agents when diluted with nitrogen, and the order of reactivity follows:



Like most halogen fluorides, ClF , ClF_3 and ClF_5 all react with strong bases (e.g., alkali metal fluorides) to form anions, (10.3.12) and (10.3.13), and strong acids (e.g., AsF_5 and SbF_5) to form cations, (10.3.14), (10.3.15), and (10.3.16).



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