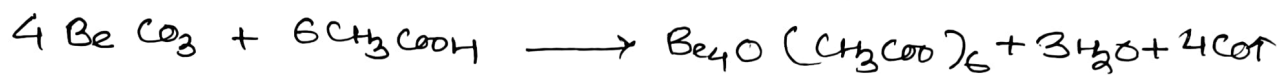
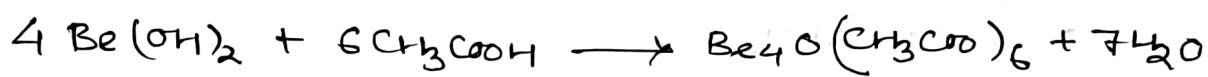


## Basic Beryllium acetate

Preparation This compound can be prepared by dissolving  $\text{Be}(\text{OH})_2$  or  $\text{BeCO}_3$  in glacial acetic acid. The resulting solution is diluted with water and then evaporated to dryness, so that a residue of  $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$  is obtained. This residue is dissolved in  $\text{CHCl}_3$ . The  $\text{CHCl}_3$  solution, on evaporation, gives the crystals of  $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$ .

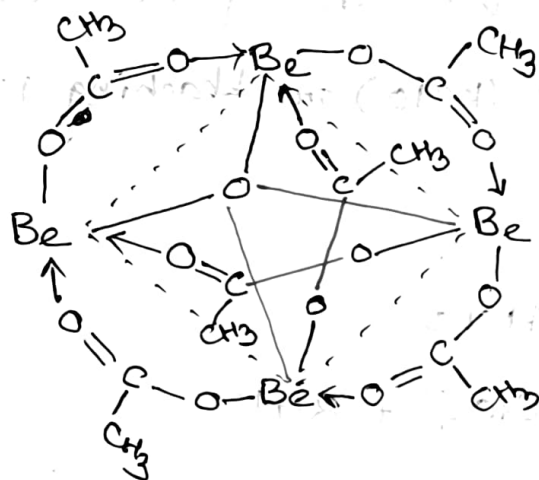


- Uses
- (i) For the preparation of other beryllium salts
  - (ii) For purifying beryllium metal by solvent extraction method.

Structure X-ray diffraction of this salt has shown that  $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$  molecule has tetrahedral shape whose centre is occupied by O-atom and the four corners are being occupied by four beryllium atoms. Six acetate groups, are arranged along the six edges of the tetrahedron.

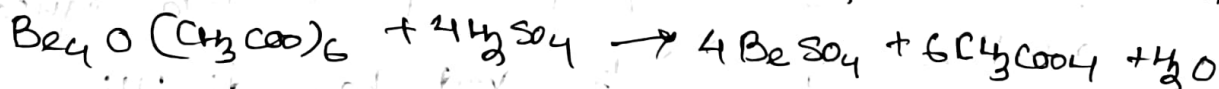
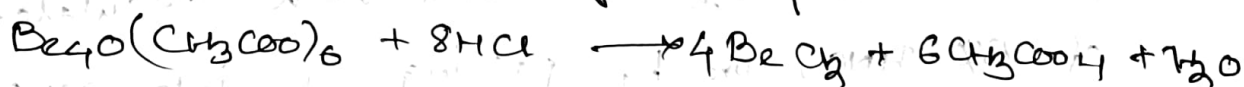
The structure clearly indicates that each Be atom is covalently attached with O-atoms of three  $\text{CH}_3\text{COO}^-$  groups. The central O atom is linked with four Be atoms. It may be noted that although Be- and O-atoms are normally bivalent, but in

$\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$  molecule, both of these are tetra-covalent.



### Properties

1.  $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$  is a crystalline solid with m.p.  $283^\circ\text{C}$  and b.p.  $330^\circ\text{C}$ .
2. It is insoluble in water but soluble in organic solvents, like acetic acid,  $\text{CHCl}_3$ , diethyl ether.
3. It is a covalent compound and slowly hydrolysed by boiling water.
4. It reacts with mineral acids ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  etc.) and forms corresponding beryllium salts.

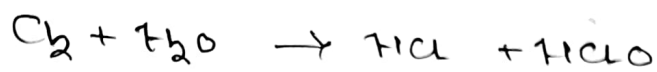


## Oxoacids of Chlorine

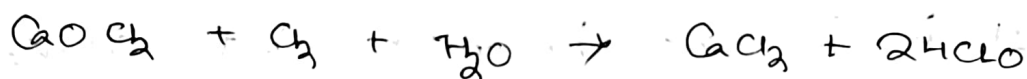
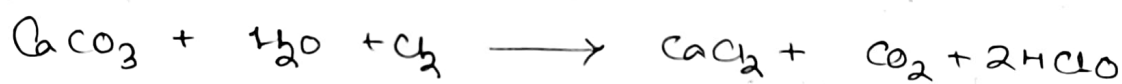
Hypochlorous acid,  $\text{HClO}$

This acid is known only in solution.  $\text{HClO}$  is prepared:

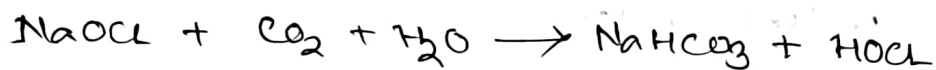
a. By passing  $\text{Cl}_2$  into  $\text{H}_2\text{O}$  or into a suspension of  $\text{CaCO}_3$  in water or into an aqueous solution of potassium hypochlorite ( $\text{KClO}$ ) or bleaching powder ( $\text{CaOCl}_2$ ).



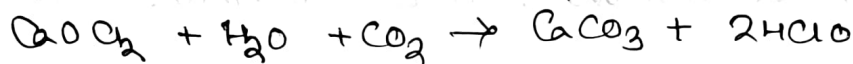
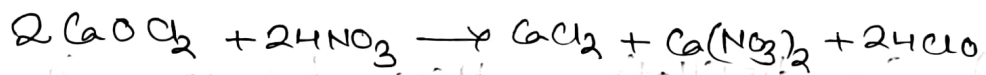
In this reaction  $\text{Cl}_2$  undergoes disproportionation into  $\text{HCl}$  and  $\text{HClO}$ .



b. By the action of atmospheric  $\text{CO}_2$  on sodium hypochlorite,  $\text{NaOCl}$



c. By distilling the aqueous solution of bleaching powder  $\text{CaOCl}_2$  with calculated quantity of 5%  $\text{HNO}_3$  or by passing  $\text{CO}_2$  into aqueous solution of  $\text{CaOCl}_2$  and then distilling.



d. By shaking  $\text{Cl}_2$  water, with freshly precipitated

$\text{HgO}$



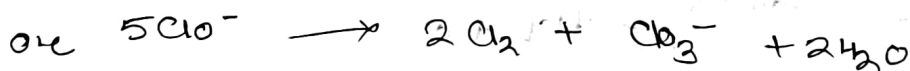
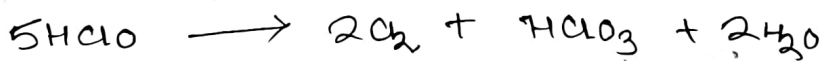
The insoluble  $\text{HgCl}_2 \cdot \text{HgO}$  is removed by filtration.

The filtrate is distilled when dilute  $\text{HClO}$  passes over.

### Properties

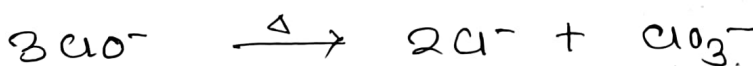
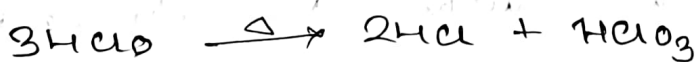
(i) The concentrated solution of  $\text{HClO}$  is yellow in colour, while the dilute solution is colourless. It is a weak acid, even weaker than  $\text{H}_2\text{CO}_3$ . Its dissociation constant is  $3 \times 10^{-8}$  at  $20^\circ\text{C}$ .

(ii) Disproportionation of the acid (a) The dilute solution of the acid is fairly stable in the dark, but when concentrated solution is exposed to light, it becomes unstable and hence undergoes disproportionation into  $\text{Cl}_2$  ( $\text{Cl} = 0$ ) and  $\text{HClO}_3$  ( $\text{Cl} = +5$ ).

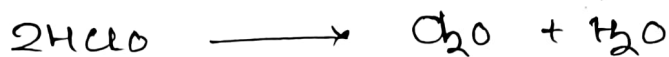


The decomposition is accelerated by Pt. black,  $\text{MnO}$  and  $\text{CoO}$ .

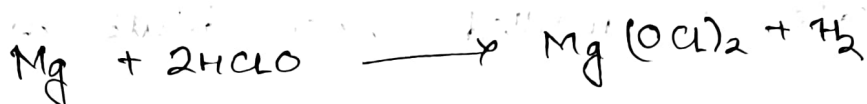
(b) When aqueous solution of  $\text{HClO}$  is heated, it undergoes disproportionation into  $\text{HCl}$  and  $\text{HClO}_3$ .



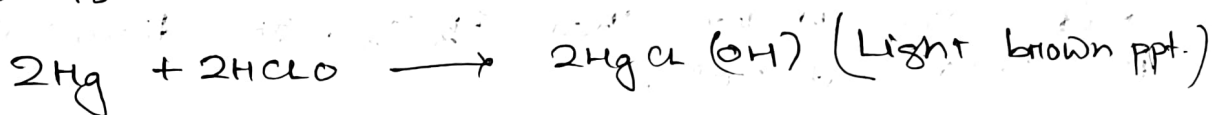
(iii) On distillation,  $\text{HClO}$  decomposes into  $\text{H}_2\text{O}$  and  $\text{Cl}_2$ .



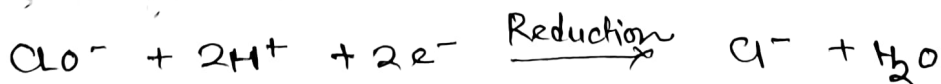
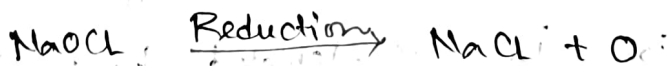
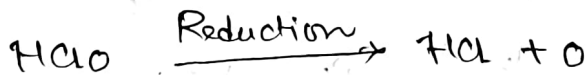
(iv) Action on metals:  $\text{HClO}$  dissolves in  $\text{Mg}$ , with the evolution of  $\text{H}_2$ ; in  $\text{Fe}$  and  $\text{Al}$ , with the evolution of  $\text{H}_2$  and  $\text{Cl}_2$ , while with  $\text{Co}$ ,  $\text{Ni}$  and  $\text{Cu}$ ,  $\text{Cl}_2$  and  $\text{O}_2$  are evolved.



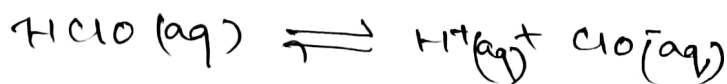
When  $\text{HClO}$  is shaken with  $\text{Hg}$ , a light brown ppt. of basic mercuric chloride,  $\text{HgCl}(\text{OH})$ , which is soluble in  $\text{HCl}$ , is obtained.



(v) Oxidising and bleaching properties: The aqueous solution of  $\text{HClO}$  and its salts (eg.  $\text{NaOCl}$ ) are oxidising and bleaching agents. This property is due to the fact that  $\text{HClO}$  or  $\text{NaOCl}$  decomposes to give nascent oxygen.

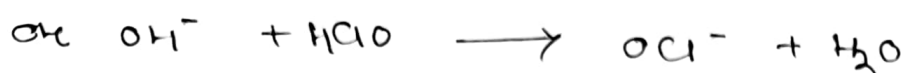


(vi) Acidic nature: Monobasic nature:  $\text{HClO}$  is a monobasic acid since its aqueous solution gives only one  $\text{H}^+$  ion on ionisation.

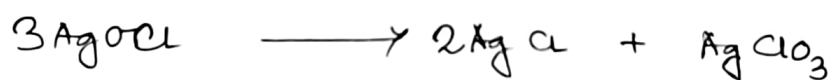


$\text{ClO}^-$  ion is called hypochlorite ion.

Its monobasic nature shows that  $\text{HClO}$  molecule has one  $\text{OH}$  group attached directly with the central  $\text{Cl}$  atom. Being an acid  $\text{HClO}$  reacts with alkalis to form the salts which are called hypochlorites, e.g.



(vii) Action of  $\text{AgNO}_3$   $\text{HClO}$  reacts with  $\text{AgNO}_3$  and gives silver hypochlorite ( $\text{AgClO}$ ). This compound is unstable and hence undergoes disproportionation into  $\text{AgCl}$  and  $\text{AgClO}_3$



## Chlorous acid, $\text{HClO}_2$

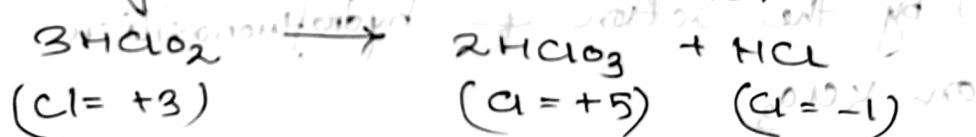
Preparation This acid is obtained in the aqueous solution by treating a suspension of  $\text{Ba}(\text{ClO}_2)_2$  with dil.  $\text{H}_2\text{SO}_4$  and filtering off the ppt. of  $\text{BaSO}_4$ . The acid can also be obtained by the action of  $\text{ClO}_2$  and  $\text{H}_2\text{O}_2$ .



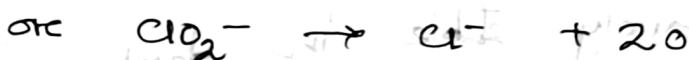
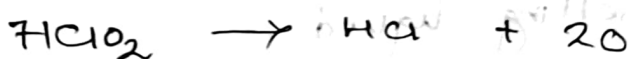
Properties (i) The freshly prepared solution of the acid is colourless but it soon decomposes to  $\text{ClO}_2$  which colours the solution yellow.

(ii) The acid gives a violet colour with  $\text{FeSO}_4$ .

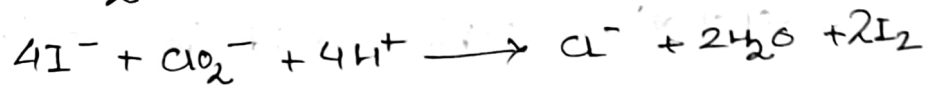
(iii)  $\text{HClO}_2$  and its salts undergo disproportionation on heating in alkaline solution.



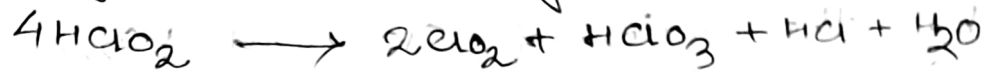
(iv)  $\text{HClO}_2$  and its salts both show oxidising properties. When they oxidise a certain substance, they are reduced to chlorides.



$\text{HClO}_2$  and its salts liberates  $\text{I}_2$  from  $\text{KI}$  solution.



(v) In acid solution,  $\text{HClO}_2$  rapidly decomposes according to the following equation:



### Chloric acid, $\text{HClO}_3$

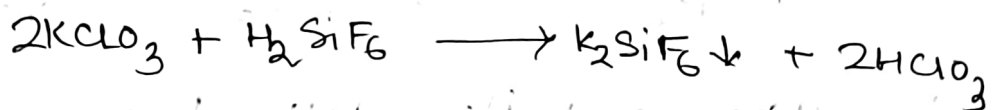
This acid is known only in solution.

It is prepared,

(i) by the action of dil  $\text{H}_2\text{SO}_4$  on  $\text{Ba}(\text{ClO}_3)_2$



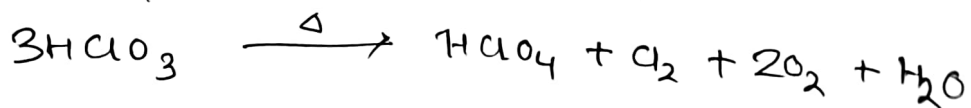
(ii) by the action of hydrofluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ) on  $\text{KClO}_3$



### Properties

(i) Conc. solution of the acid is colourless and pungent smelling liquid.

(ii) It is fairly stable in dark. In light it decomposes and becomes yellow. On heating it decomposes to give  $\text{HClO}_4$ .





(iii) When organic substances like cotton, wool, paper etc., come in contact with the acid, they catch fire.

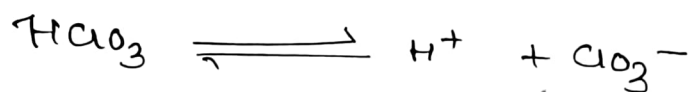
(iv) The acid is a powerful oxidising and bleaching agent.

(v) When iodine is evaporated with 25%  $\text{HClO}_3$ , iodic acid ( $\text{HIO}_3$ ) is obtained.



The reaction is used for the preparation of  $\text{HIO}_3$ .

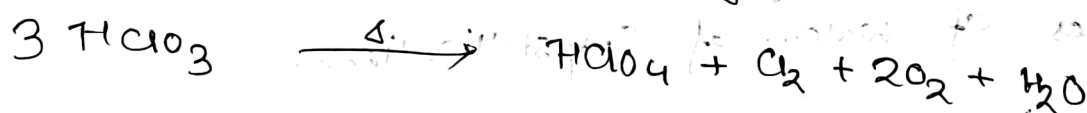
(vi)  $\text{HClO}_3$  is a monobasic acid.



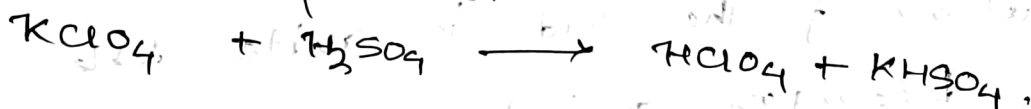
perchloric acid,  $\text{HClO}_4$

Preparation

(i) It is prepared by heating  $\text{HClO}_3$

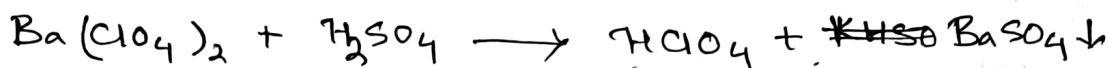


(ii) Anhydrous acid is obtained by distilling a mixture of potassium perchlorate with conc.  $\text{H}_2\text{SO}_4$  under reduced pressure.

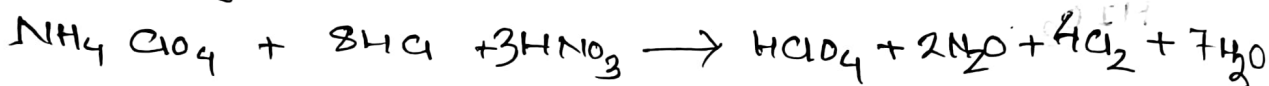


(iii) An aqueous solution of the acid is obtained!

(a) by treating  $Ba(ClO_4)_2$  with calculated quantity of dil.  $H_2SO_4$  and then removing the insoluble  $BaSO_4$  by filtration.



(b) by adding  $NH_4ClO_4$  dissolved in conc.  $HCl$  to warm conc. solution of  $HNO_3$  and then evaporating.



### Properties

(i) Anhydrous  $HClO_4$  is a colourless mobile hygroscopic and oily liquid. It fumes strongly in moist air and dissolves in water with a hissing sound due to the liberation of heat.

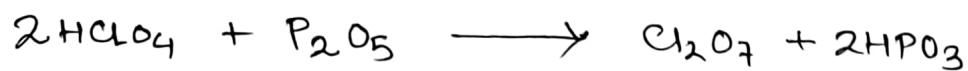
(ii) It forms hydrates with 1, 2, 2.5, 3 and 3.5 molecules of water of crystallisation.

(iii) It is unstable and decomposes with explosion on heating, and sometimes merely on standing for a few days even in the dark. Aqueous solution of the acid is quite stable and does not decompose and hence can be kept indefinitely.

(iv) It is highly dangerous acid and produces severe wounds on the skin.

(v) It is a powerful oxidising agent and inflames paper and wood.

(vi) On dehydration with  $P_2O_5$  at  $-10^\circ C$ , it gives  $Cl_2O_7$  which is the anhydride of perchloric acid.



This reaction has been used for the preparation of  $Cl_2O_7$ .

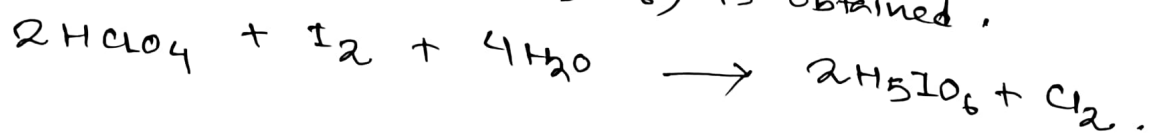
(vii)  $HClO_4$  is the strongest acid of all the acids.

(viii) The metal like Zn, Fe etc. dissolve in the aqueous solution of the acid and form the soluble perchlorates.



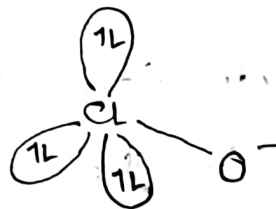
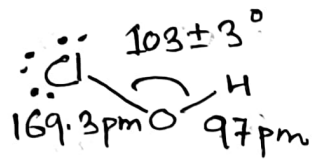
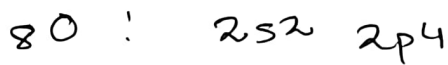
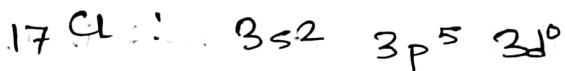
(ix) The acid is not reduced by nascent hydrogen but is reduced to chloride by strong reducing agents like  $SnCl_2$ ,  $CuCl_2$  etc.

(x) When a suspension of iodine is heated with  $HClO_4$ , paraperiodic acid ( $H_5IO_6$ ) is obtained.



## Structures

### HClO

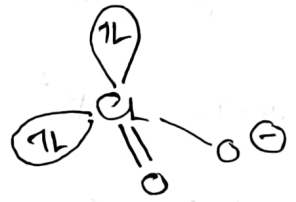
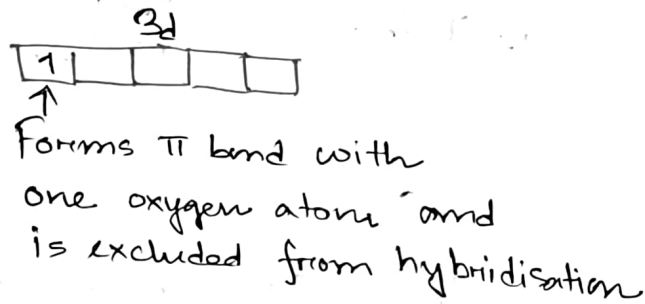
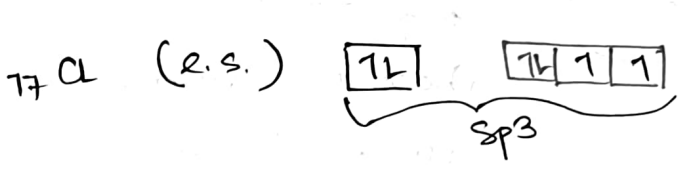
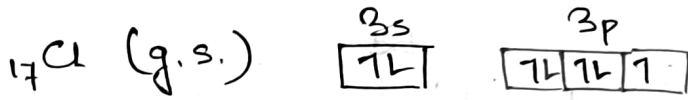
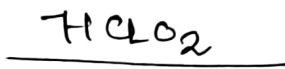


One  $3s$  and three  $3p$  orbitals of Cl atom hybridises to give four  $sp^3$  hybrid orbitals.

Three  $sp^3$  hybrid orbitals contain the lone pair of electrons while the fourth one contains unpaired electron. One  $sp^3$  hybrid orbital containing one unpaired electron overlaps with  $p$ -orbital of O atom to form  $sp^3 - p$  sigma bond. Also  $\pi - \pi$  bond by the overlap of full  $2p$  orbital on oxygen and empty  $d$  orbital on chlorine.

$s$  orbital of H atom overlaps with  $p$ -orbital of O to form  $s - p$  sigma bond. Thus three  $sp^3$  hybrid orbitals containing lone pair of electrons and one  $O - O - H$  bond are directed towards four corners of a regular tetrahedron to form a 'V' shape.

The structure of  $ClO^-$  ion is linear



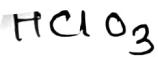
The electron configuration of Cl atom is shown above. One 3s and three 3p orbitals hybridise to give four sp<sup>3</sup> hybrid orbitals. Two sp<sup>3</sup> hybrid orbitals are occupied by two lone pairs and the other two are occupied by two unpaired electrons.

The two half filled sp<sup>3</sup> hybrid orbitals overlap with 2p orbitals (with one electron) from 2<sup>o</sup> O atom to form two sp<sup>3</sup>-p 'σ' bonds.

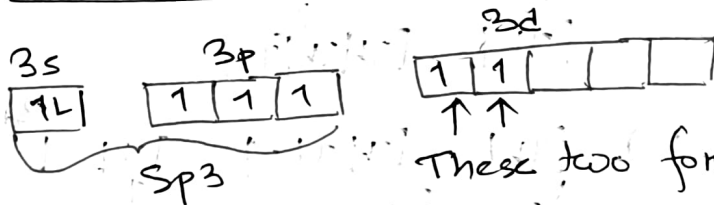
The H atom's s orbital overlaps with the half filled 'p' orbital of one 'O' atom.

The unhybridised 'd' orbital of Cl overlaps with one half filled 'p' orbital of one the other oxygen to form a pπ-dπ bond.

The shape of ClO<sub>2</sub><sup>-</sup> is 'V' shaped.



17 Cl (e. s.)



These two forms  
p $\pi$ -d $\pi$  bonds.

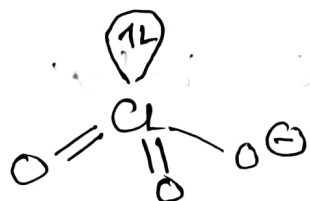
One 3s and three 3p orbitals of Cl hybridise to form four sp<sup>3</sup> hybrid orbitals. Two 3d orbitals remain unhybridised.

One sp<sup>3</sup> hybrid orbital contains the lone pair.

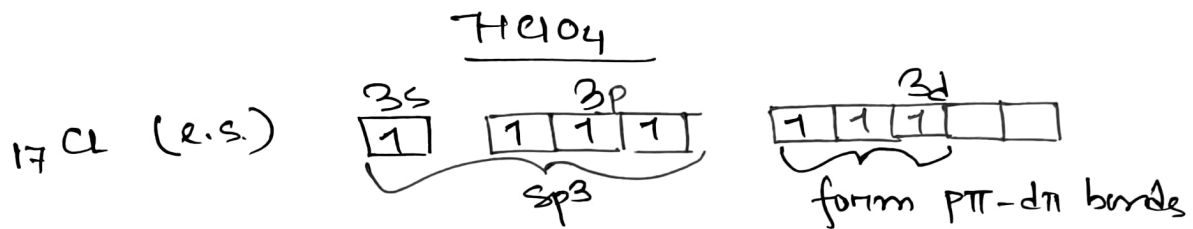
Other three sp<sup>3</sup> hybrid orbitals contain 1 unpaired electron each and overlap with three 2p orbitals (half filled) of three O atoms to form three sp<sup>3</sup>-p  $\sigma$  bonds.

Two of the half filled 'p' orbitals from two O atoms overlap with two 3d orbitals of Cl to form 2  $\pi$  p $\pi$ -d $\pi$  bonds.

One 'p' orbital from the remaining O atom overlaps with 1s orbital of the H atom.



The structure of ClO<sub>3</sub><sup>-</sup> is pyramidal.

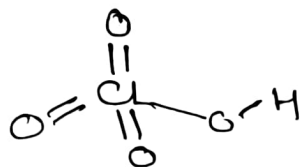


one 3s and three 3p orbitals of Cl overlap to form three four sp<sup>3</sup> hybrid orbitals containing one electron each.

All the sp<sup>3</sup> hybrid orbitals overlap with four 2p orbitals (half filled) of four 'O' atoms to form four sp<sup>3</sup>-p σ bonds.

Three 2p orbitals from three of the 'O' atoms overlap with three 3d orbitals (that do not take part in hybridisation) of Cl to form three π-dπ bonds.

The 2p orbital of the remaining 'O' atom overlap with the 1s orbital of the 'H' atom.



The structure of ClO<sub>4</sub><sup>-</sup> is tetrahedral.