Zinc chloride

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Zinc chloride is the name of chemical compounds with the formula $ZnCl_2$ and its hydrates. Zinc chlorides, of which nine crystalline forms are known, are colorless or white, and are highly soluble in water.[citation needed] $ZnCl_2$ itself is hygroscopic and even deliquescent. Samples should therefore be protected from sources of moisture, including the water vapor present in ambient air. Zinc chloride finds wide application in textile processing, metallurgical fluxes, and chemical synthesis. No mineral with this chemical composition is known aside from the very rare mineral simonkolleite, $Zn_5(OH)_8Cl_2 \cdot H_2O$.

Contents

Structure and properties

Four crystalline forms (polymorphs) of $ZnCl_2$ are known: α, β, γ, and δ, and in each case the Zn^{2+} ions are tetrahedrally coordinated to four chloride ions.[1]

Form	Symmetry	Pearson symbol	Group	No	a (nm)	b (nm)	c (nm)	Z	ρ (g/cm^3)
α	Tetragonal	tI12	$I\bar{4}2d$	122	0.5398	0.5398	0.64223	4	3.00
β	Tetragonal	tP6	$P4_2/nmc$	137	0.3696	0.3696	1.071	2	3.09
γ	Monoclinic	mP36	$P2_1c$	14	0.654	1.131	1.23328	12	2.98
δ	Orthorhombic	oP12	$Pna2_1$	33	0.6125	0.6443	0.7693	4	2.98

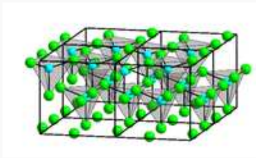
Here, a, b, and c are lattice constants, Z is the number of structure units per unit cell and ρ is the density calculated from the structure parameters.[2][3][4]

The pure anhydrous orthorhombic form (δ) rapidly changes to one of the other forms on exposure to the atmosphere and a possible explanation is that the OH^- ions originating from the absorbed water facilitate the rearrangement.[1] Rapid cooling of molten $ZnCl_2$ gives a glass, that is, a rigid amorphous solid and this ability has been related to the structure in the melt.[5]

The covalent character of the anhydrous material is indicated by its relatively low melting point of 275 °C.[6] Further evidence for covalency is provided by the high solubility of the dichloride in ethereal solvents where it forms adducts with the formula $ZnCl_2L_2$, where L = ligand such as $O(C_2H_5)_2$. In the gas phase, $ZnCl_2$ molecules are linear with a bond length of 205 pm.[7]

Molten $ZnCl_2$ has a high viscosity at its melting point and a comparatively low electrical conductivity that increases markedly with temperature.[7][8] A Raman scattering study of the melt indicated the presence of polymeric structures [9] and a neutron scattering study indicated the presence of tetrahedral $\{ZnCl_4\}$ complexes.[10]

Zinc chloride



IUPAC name

Zinc chloride

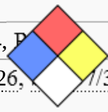
Other names

Zinc(II) chloride
Zinc dichloride
Butter of zinc

Identifiers	
CAS number	7646-85-7 ✓
PubChem	3007855
ChemSpider	5525 ✓
UNII	86Q357L16B ✓
EC number	231-592-0
UN number	2331
ChEBI	CHEBI:49976 ✓
ChEMBL	CHEMBL1200679 ✗
RTECS number	ZH1400000
ATC code	B05XA12 (http://www.whocc.no/atc_ddd_index/?code=B05XA12)
Jmol-3D images	Image 1 (http://chemapps.stolaf.edu/jmol/jmol.php?model=Cl%5BZn%5DCl)
SMILES	
InChI	
Properties	
Molecular formula	$ZnCl_2$
Molar mass	136.315 g/mol
Appearance	white crystalline solid hygroscopic
Odor	odorless
Density	2.907 g/cm^3
Melting point	292 °C (558 °F; 565 K)
Boiling point	756 °C (1,393 °F; 1,029 K)
Solubility in water	4320 g/L (25 °C)
Solubility	soluble in ethanol, glycerol and acetone
Solubility in alcohol	4300 g/L
Structure	
Coordination geometry	Tetrahedral, linear in the gas phase

Hydrates

Five hydrates of zinc chloride are known, $ZnCl_2(H_2O)_n$ where n = 1, 1.5, 2.5, 3 and 4.[11] The tetrahydrate $ZnCl_2(H_2O)_4$ crystallizes from aqueous solutions of zinc chloride.[11]

Hazards	
MSDS	External MSDS (http://physchem.ox.ac.uk/MSDS/ZI/zinc_chloride.html)
EU Index	030-003-00-2
EU classification	Harmful (**Xn**) Corrosive (**C**) Dangerous for the environment (**N**)
R-phrases	R22, R34, R
S-phrases	(S1/2), S26, //39, S45, S60, S61
NFPA 704	 0 3 0
LD_{50}	350 mg/kg, rat (oral)
Related compounds	
Other anions	Zinc fluoride Zinc bromide Zinc iodide
Other cations	Cadmium chloride Mercury(II) chloride
Except where noted otherwise, data are given for materials in their standard state (at 25 °C (77 °F), 100 kPa)	
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Infobox references	

Preparation and purification

Anhydrous $ZnCl_2$ can be prepared from zinc and hydrogen chloride.

$$Zn(s) + 2\ HCl \rightarrow ZnCl_2 + H_{2(g)}$$

Hydrated forms and aqueous solutions may be readily prepared similarly by treating Zn metal with hydrochloric acid. Zinc oxide and zinc sulfide react with HCl:

$$ZnS(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2S(g)$$

Unlike many other elements, zinc essentially exists in only one oxidation state, 2+, which simplifies purification of the chloride.

Commercial samples of zinc chloride typically contain water and products from hydrolysis as impurities. Such samples may be purified by recrystallization from hot dioxane . Anhydrous samples can be purified by sublimation in a stream of hydrogen chloride gas, followed by heating the sublimate to 400 °C in a stream of dry nitrogen gas. Finally, the simplest method relies on treating the zinc chloride with thionyl chloride.[12]

Reactions

Molten anhydrous $ZnCl_2$ at 500–700 °C dissolves zinc metal, and, on rapid cooling of the melt, a yellow diamagnetic glass is formed, which Raman studies indicate contains the Zn_2^{2+} ion.[11]

A number of salts containing the tetrachlorozincate anion, $ZnCl_4^{2-}$, are known.[7] "Caulton's reagent," $V_2Cl_3(thf)_6Zn_2Cl_6$ is an example of a salt containing $Zn_2Cl_6^{2-}$.[13][14] The compound Cs_3ZnCl_5 contains tetrahedral $ZnCl_4^{2-}$ and Cl^- anions.[1] No compounds containing the $ZnCl_6^{4-}$ ion have been characterized.[1]

Whilst zinc chloride is very soluble in water, solutions cannot be considered to contain simply solvated Zn^{2+} ions and Cl^- ions, $ZnCl_xH_2O_{(4-x)}$ species are also present.[15][16][17] Aqueous solutions of $ZnCl_2$ are acidic: a 6 M aqueous solution has a pH of 1.[11] The acidity of aqueous $ZnCl_2$ solutions relative to solutions of other Zn^{2+} salts is due to the formation of the tetrahedral chloro aqua complexes where the reduction in coordination number from 6 to 4 further reduces the strength of the O-H bonds in the solvated water molecules.[18]

In alkali solution in the presence of OH^- ion various zinc hydroxychloride anions are present in solution, e.g.$ZnOH_3Cl^{2-}$, $ZnOH_2Cl_2^{2-}$, $ZnOHCl_3^{2-}$, and $Zn_5OH_2Cl_3 \cdot H_2O$ (simonkolleite) precipitates.[19]

When ammonia is bubbled through a solution of zinc chloride the hydroxide does not precipitate, instead compounds containing complexed ammonia (ammines) are produced, $Zn(NH_3)_4Cl_2 \cdot H_2O$ and on concentration $ZnCl_2(NH_3)_2$.[20] The former contains the $Zn(NH_3)_6^{2+}$ ion [1] and the latter is molecular with a distorted tetrahedral geometry.[21] The species in aqueous solution have been investigated and show that $Zn(NH_3)_4^{2+}$ is the main species present with $Zn(NH_3)_3Cl^+$ also present at lower NH_3:Zn ratio.[22]

Aqueous zinc chloride reacts with zinc oxide to form an amorphous cement that was first investigated in the 1855 by Stanislas Sorel. Sorel later went on to investigate the related magnesium oxychloride cement, which bears his name.[23]

When hydrated zinc chloride is heated, one obtains a residue of Zn(OH)Cl e.g.[24]

$$ZnCl_2 \cdot 2H_2O \rightarrow ZnCl(OH) + HCl + H_2O$$

The compound $ZnCl_2 \cdot ½HCl \cdot H_2O$ may be prepared by careful precipitation from a solution of $ZnCl_2$ acidified with HCl and it contains a polymeric anion $(Zn_2Cl_5{}^-)_n$ with balancing monohydrated hydronium ions, $H_5O_2{}^+$ ions.[1][25]

The formation of highly reactive anhydrous HCl gas formed when zinc chloride hydrates are heated is the basis of qualitative inorganic spot tests.[26]

The use of zinc chloride as a flux, sometimes in a mixture with ammonium chloride (see also Zinc ammonium chloride), involves the production of HCl and its subsequent reaction with surface oxides. Zinc chloride forms two salts with ammonium chloride, $(NH_4)ZnCl_4$ and $(NH_4)_3ClZnCl_4$, which decompose on heating liberating HCl just as zinc chloride hydrate does. The action of zinc chloride/ammonium chloride fluxes, for example, in the hot dip galvanizing process produces H_2 gas and ammonia fumes.[27]

Cellulose dissolves in aqueous solutions of $ZnCl_2$ and zinc-cellulose complexes have been detected.[28] Cellulose also dissolves in molten $ZnCl_2$ hydrate and carboxylation and acetylation performed on the cellulose polymer.[29]

Thus, although many zinc salts have different formulas and different crystal structures, these salts behave very similarly in aqueous solution. For example, solutions prepared from any of the polymorphs of $ZnCl_2$ as well as other halides (bromide, iodide) and the sulfate can often be used interchangeably for the preparation of other zinc compounds. Illustrative is the preparation of zinc carbonate:

$$ZnCl_2(aq) + Na_2CO_3(aq) \rightarrow ZnCO_3(s) + 2\ NaCl(aq)$$

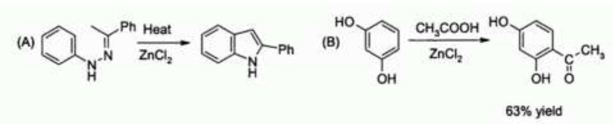
Applications

As a metallurgical flux

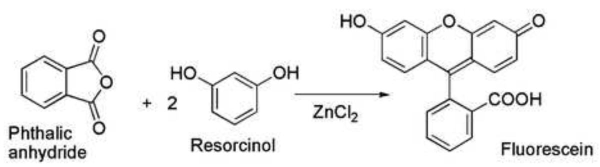
Zinc chloride has the ability to react with metal oxides (MO) to give derivatives of the formula $MZnOCl_2$.[30]This reaction is relevant to the utility of $ZnCl_2$ solution as a flux for soldering — it dissolves oxide coatings exposing the clean metal surface.[30] Fluxes with $ZnCl_2$ as an active ingredient are sometimes called "tinner's fluid". Typically this flux was prepared by dissolving zinc foil in dilute hydrochloric acid until the liquid ceased to evolve hydrogen; for this reason, such flux was once known as "killed spirits". Because of its corrosive nature, this flux is not suitable for situations where any residue cannot be cleaned away, such as electronic work. This property also leads to its use in the manufacture of magnesia cements for dental fillings and certain mouthwashes as an active ingredient.

In organic synthesis

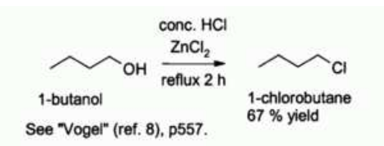
In the laboratory, zinc chloride (Silzic) finds wide use, principally as a moderate-strength Lewis acid. It can catalyze (A) the Fischer indole synthesis,[31] and also (B) Friedel-Crafts acylation reactions involving activated aromatic rings[32][33]



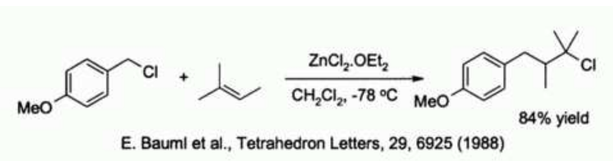
Related to the latter is the classical preparation of the dye fluorescein from phthalic anhydride and resorcinol, which involves a Friedel-Crafts acylation.[34] This transformation has in fact been accomplished using even the hydrated $ZnCl_2$ sample shown in the picture above.



Hydrochloric acid alone reacts poorly with primary alcohols and secondary alcohols, but a combination of HCl with $ZnCl_2$ (known together as the "Lucas reagent") is effective for the preparation of alkyl chlorides. Typical reactions are conducted at 130 °C. This reaction probably proceeds via an S_N2 mechanism with primary alcohols but S_N1 pathway with secondary alcohols.

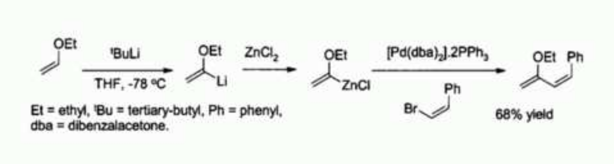


Zinc chloride also activates benzylic and allylic halides towards substitution by weak nucleophiles such as alkenes:[35]

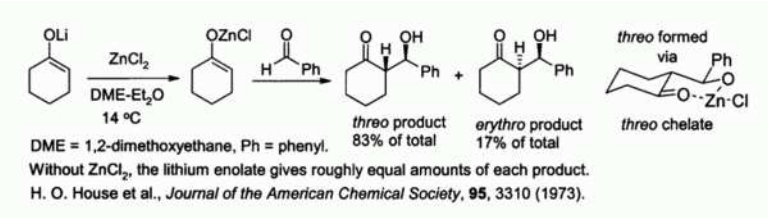


In similar fashion, $ZnCl_2$ promotes selective $NaBH_3CN$ reduction of tertiary, allylic or benzylic halides to the corresponding hydrocarbons.

Zinc chloride is also a useful starting reagent for the synthesis of many organozinc reagents, such as those used in the palladium catalyzed Negishi coupling with aryl halides or vinyl halides.[36] In such cases the organozinc compound is usually prepared by transmetallation from an organolithium or a Grignard reagent, for example:



Zinc enolates, prepared from alkali metal enolates and $ZnCl_2$, provide control of stereochemistry in aldol condensation reactions due to chelation on to the zinc. In the example shown below, the *threo* product was favored over the *erythro* by a factor of 5:1 when $ZnCl_2$ in DME/ether was used.[37] The chelate is more stable when the bulky phenyl group is pseudo-equatorial rather than pseudo-axial, i.e., *threo* rather than *erythro*.



In textile processing

Concentrated aqueous solutions of zinc chloride (more than 64% weight/weight zinc chloride in water) have the interesting property of dissolving starch, silk, and cellulose. Thus, such solutions cannot be filtered through standard filter papers. Relevant to its affinity for these materials, $ZnCl_2$ is used as a fireproofing agent and in fabric "refresheners" such as Febreze.

Smoke grenades

The zinc chloride smoke mixture ("HC") used in smoke grenades contains zinc oxide and hexachloroethane, which, when ignited, react to form zinc chloride smoke, an effective smoke screen.[38]

Fingerprint detection

Ninhydrin reacts with amino acids and amines to form a colored compound “Ruhemann’s purple” (RP). Spraying with a zinc chloride solution forms a 1:1 complex RP:$ZnCl(H_2O)_2$, which is more readily detected as it fluoresces better than Ruhemann’s purple.[39]

Disinfectant

Historically, a dilute aqueous solution of zinc chloride was used as a disinfectant under the name "Burnett's Disinfecting Fluid". [40] It is also used in some commercial brands of antiseptic mouthwash.

Safety considerations

Zinc chloride is a skin and respiratory irritant according to its MSDS.[41] Precautions that apply to anhydrous $ZnCl_2$ are those applicable to other anhydrous metal halides, i.e. hydrolysis can be exothermic and contact should be avoided. Concentrated solutions are acidic and corrosive, and specifically attack cellulose and silk as Lewis acids.[42]

Zinc chloride fume has occupational exposure limits set, as the Occupational Safety and Health Administration and the National Institute for Occupational Safety and Health have both set limits at 1 mg/m^3 over an eight time-weighted average. A short-term exposure limit for exposure is set at 2 mg/m^3.[43] An Immediately Dangerous to Life and Health exposure is set at 50 mg/m^3.[44]

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External links

- Grades and Applications of Zinc Chloride (http://muby.itgo.com/zincchloride.html)

- PubChem $ZnCl_2$ summary (http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=5727).

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