

Chapter 1

Introduction

Solid materials can be classified according to a variety of criteria. Among the most significant of these is the description of a solid as being either crystalline or amorphous. Large natural crystals of a variety of solids have been known to man for thousands of years. Typical examples are quartz (SiO_2), rock salt (NaCl) the sulphides of metals such as lead and zinc and of course gemstones such as ruby (Al_2O_3) and diamond (C).

For many centuries the word “crystal” was applied specifically to quartz, it is based on the Greek word implying a form similar to that of ice. In current usage, a crystalline solid is one in which the atomic arrangement is regularly repeated and which is likely to exhibit an external morphology of planes making characteristic angles with each other if the sample being studied happens to be a single crystal. When two single crystals of the same solid are compared, it will usually be found that the sizes of the characteristic plane “faces” are not in the same proportion the “habit” varies from crystal to crystal”. On the other hand, the interfacial angles are always the same for crystals of a given material.

The transition metal represents the filling of the atomic d-electron shell. Because the transition metals and their alloys typically have high melting temperature and hardness, their economic importance is immense. There has been rather little experimental work on phase transitions in transition metals because these elements are relatively incompressible yielding phase changes only at very high pressures beyond the experimental range.

Salen is the abbreviation for a popular chelating ligand used in coordination chemistry and homogeneous catalysis. The name salen is a contraction for salicylic aldehyde and ethylenediamine. The ligand is a bright yellow micaceous solid that is soluble in polar organic solvents. The diphenol $H_2\text{salen}$ is the conjugate acid of the ligand that logically is salen^{2-} . But the terminology is used loosely. As an anionic tetradentate ligand, salen^{2-} resembles tetradentate ligands including those that are macrocyclic, such as porphyrinate, corrin, bis(dimethylglyoximate), and some Schiff bases.

SalenH_2 is commercially available. It was first prepared by Pfeiffer[1]. It is often generated in situ followed by the addition of the metal salt, but the ligand is also easily prepared as a pure organic compound by the condensation of ethylenediamine and salicylaldehyde[2].

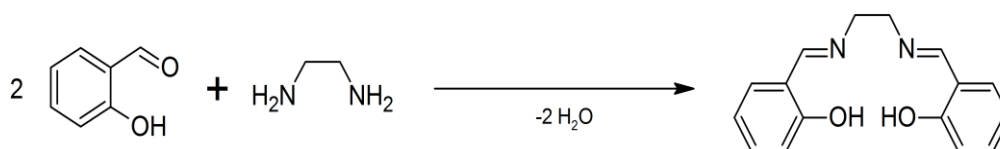


Figure 1.1 Salen H₂

In 1938, T. Tsumaki reported that the cobalt(II) salen reversibly bound O_2 , and this finding led to intensive research on cobalt complexes salen and related ligands for the storage and transport of oxygen, i.e. synthetic oxygen carriers[3]. SalenH_2 forms complexes with most transition metals. In many cases, the metal adopts square pyramidal or octahedral coordination sphere with the stoichiometry $M(\text{salen})L$ and $M(\text{salen})L_2$. Illustrative examples include $VO(\text{salen})$ and $Co(\text{salen})Cl(\text{pyridine})$. With d^8 metal ions, low-spin square planar complexes form, such as $Ni(\text{salen})$.

- The ligand acacen (parent: H₂acacen) is derived by condensation of acetylacetone and ethylenediamine.
- The ligand abbreviated "Salph" is derived from the condensation of 1,2-phenylenediamine and salicylaldehyde.
- The ligand "Salqu," derived by condensation of salicylaldehyde and 2-quinoxalinol, is an anionic tetradentate ligand, reminiscent of other macrocyclic ligands. Salqu copper complexes have been investigated as oxidation catalysts[4].

Chiral versions the salen motif are derived from chiral 1,2-diamines. For example, condensation of the C₂-symmetric trans-1,2-diaminocyclohexane with 3,5-di-tert-butylsalicylaldehyde gives a ligand that forms complexes with Cr, Mn, Co, Al, which have proven useful for asymmetric transformations. For an example, see the Jacobsen epoxidation[5].

Salen (N,N-bis-salicylidene-ethylenediamine) is a tetradentate chelate ligand providing two nitrogen and two oxygen donor atoms to coordinate a metal in a square planar or slightly distorted (D_{2d}) square-planar fashion.[6] Thereby it shares similarities with porphyrine-type ligands but is much easier to synthesize and handle. The basic salen ligand 19 is synthesized by the condensation of two salicylic aldehyde molecules 20 with one molecule ethylenediamine 21 resulting in the formation of two Schiff-base moieties (Figure 1.2).

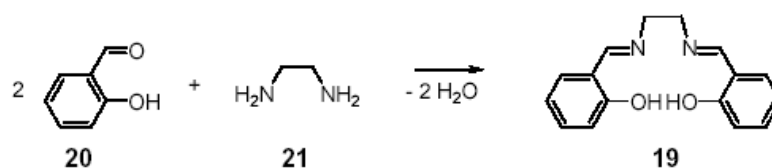


Figure: 1.2 Synthesis of the salen ligand.

The assembly of the ligand usually occurs spontaneously[7] and may also be promoted by a metal template.[8] The use of numerous differently substituted salicylic aldehyde derivatives as well as different chiral ethylenediamines and longer-chain diamines has been reported to create a plethora of chiral and non-chiral ligands with preferences for different metals and solvents.[7] The variety of coordinated metal ions is expressed by the vast number of references that can be found for metal-salen complexes in chemical databases: for each of about 20 different metals more than 100 publications are available, with Co, Mn, Cu, Ni, Fe, Cr and V as the most prominent metals that were studied.[8] Metal salen complexes of these elements are widely used in catalysis. Because of the high versatility and fidelity of salen complexes they have been ranked among the “privileged ligands for catalysis” by *Jacobsen*. [8]

The most prominent application of salen complexes is the asymmetric epoxidation of unfunctionalized alkenes, which was independently developed by *Eric Jacobsen* and *Tsutomu Katsuki* in 1990.[8, 9] Chromium and manganese are the metals mainly used as catalytically active metals in the epoxidation catalysts and the topic has been extensively reviewed.[10] Examples for other reactions catalyzed by salen complexes are cyclopropanations,[11] oxidations[12] and kinetic resolutions.[13]

Properties of Salen

Table 1.1 Properties of Salen

Identifiers	
CAS number	94-93-9
Properties	
Molecular formula	C ₁₆ H ₁₆ N ₂ O ₂
Molar mass	268.31
Appearance	yellow solid
Melting point	125-129 °C, 269 K, -75 °F
Solubility in water	organic solvents

1.1 Crystal growth

In case of materials which decompose or sublime before melting at atmospheric pressure and a suitable solvent is not available, crystals can often be grown conveniently from the vapour phase technique. Such materials hence cannot be easily grown from the solution or melt methods. Since transition metal dichalcogenides belongs to these family of materials, vapour phase method has been employed in the present work for their growth.

Leith [14-19] has given an excellent review of various methods for the preparation and crystal growth of transition metal dichalcogenides. Recently, Aruchamy[20] have discussed the materials aspect of TMDC's in which a wealth of information is available on the growth of these materials. The vapour phase method used for the growth of transition metal dichalcogenides is classified into two categories viz.

- (1) Chemical Vapour Transport Technique (CVT).
- (2) Direct Vapour Transport Technique (DVT).

1.1.1 Chemical Vapour Transport Technique

This technique has been reported as a reliable method for the growth of TMDC crystals [20-25]. The technique mainly depends on a chemical reaction between the source material to be crystallized and a transporting agent. The reaction product is volatile and can be transported into the vapour phase at temperatures well below the melting point of the compound. Transport occurs between zones having different temperatures, usually the starting reaction occurs at a higher temperature and is reversed at the low temperature to deposit molecules of the compound at the most favourable crystalline sites. Initially random deposition occurs until seed crystals are formed. Thereafter, growth preferentially occurs on these seeds, and large single crystals are formed. In this method, one can transport unlimited amount of starting material with only a small amount of the transporting agent.

Nitsche et al. [21] arrived at the following conclusions for the successful growth of crystals by vapour transport technique.

1. The rate of transport must not exceed the rate of growth of seeds.
2. The optimum crystallization temperature must be evaluated empirically for each system taking into account the possibility of polymorphism.
3. The crystallization chamber should be large in order to prevent intergrowth between adjacent seeds. Asymmetric heating is sometimes useful.
4. The temperature distribution in the crystallization chamber should
be as uniform as possible to avoid partial reevaporation of already grown crystals.

5. Well-developed crystals can be formed more easily in large diameter tubes, where transporter convection determines the rate of transport.

1.1.2 Direct Vapour Transport Technique

Although, CVT technique gives large crystals, the crystals grown by this method usually incorporate small amount of the transporting agent which may remain as an active impurity and affect the measured properties. Therefore, to grow crystals without such contamination, a method of growth, which avoids the transporting agent, is found to be more satisfactory. This method is called as direct vapour transport or sublimation method. The exact growth conditions depend on the material to be grown.

1.1.3. Single crystal growth

In the case of CVT technique, the charge prepared in the manner described above is transferred into another quartz ampoule with the required amount of the transporting agent and is evacuated to a pressure of 10^{-5} torr and sealed at one end. The charge along with the transporter is kept at one end of the ampoule. The ampoule is then placed in the tube furnace. The furnace temperature in both the zones is increased slowly to the required final temperatures for growth.

After the required period of growth time, the furnace is allowed to cool down at a much slower rate upto room temperature. Similarly in the case of DVT technique, no transporting agent is used and the growth is proceeded in the same way as in the case of CVT technique.

When the ampoule is broken, shining black coloured crystals are obtained in both the cases. These are stable on exposure to air and are platelike with c-axis normal to the plane. All the crystals grew over the distributed charge inside the ampoule.

In materials science, rather than haphazardly looking for and discovering materials and exploiting their properties, the aim is instead to understand materials so that new materials with the desired properties can be created

1.2 Intercalation

Materials with layer structures, for which the bonding between the layers is of the weak vander Waals type, offer a unique opportunity for obtaining information about their electronic properties and energy band structures via experiments involving intercalation. “Intercalation” means insertion or interposing of foreign ions, atoms or molecules between the layers of these materials, a process only made possible by the weakness of the interlayer bonding. The size of the interlayer gap may either increase or decrease upon intercalation, depending upon the size of the intercalated system and nature of any bonding mechanism between this system and the host layers.

1.3 Criterion for the formation of true intercalation compounds

- The atoms in the host surfaces should be held by primary valence forces so as to form two-dimensional layers, which should be substantially rigid. Normally, bonding between these two dimensional layers so as to form three dimensional crystal

of host material should be much weaker (say $> 10\%$) than within each layer.

- Two-dimensional patterns of atoms in each (rigid) layer should show correlations with those in the perpendicular direction which might or might not be systematically changed when an intercalate penetrates between them.
- Various atoms or molecules should be able to enter between the host layers, causing them to separate.

Intercalation should be largely but not entirely reversible

The intercalation of cobalt-salen complexes into the interlamellar spaces of montmorillonite clay was investigated by various characterization studies. The “neat” cobalt-salen complex showed a weight loss at 368 °C while the weight loss for the corresponding intercalated complex was observed at much higher temperature of 492 °C due to decomposition of the complex. The thermal stabilization observed was due to the host–guest interaction of clay and metal complex and thus confirmed the intercalation. The XANES spectrum of Co(salen)-mont sample revealed the change of symmetry from the tetrahedral in plane to the octahedral structure having an axial bonding of oxygen to the cobalt, indicating that cobalt atoms in Co(salen)-mont were coordinated axially with the lattice oxygen of montmorillonite. Both XANES and EXAFS results indicated that cobalt atoms in Co(salen)-mont form two additional Co–O bonds with a bond length of 0.199 nm by the intercalation while retaining the Co-salen structure. Co-salen intercalated into the montmorillonite clay showed the highest activity for the air oxidation of *p*-cresol, giving 88% selectivity to the oxidation products. Effects of NaOH concentration and various solvents on the conversion and selectivity patterns also have been studied. [29]

Air oxidation of *p*-cresol under very mild conditions (338 K and ambient pressure) was carried out in a semibatch reactor over a solid catalyst developed by intercalating cobalt–salen into the montmorillonite clay. The intercalation of cobalt–salen was done by a simple protocol, and the characterization of the intercalated catalyst was done by XPS, FTIR, and XRD techniques. A total selectivity $\geq 90\%$ to the oxidation products could be achieved with this solid catalyst by eliminating the undesired coupling side products in air oxidation of *p*-cresol under ambient pressure conditions. Effect of various process parameters on the conversion and selectivity pattern were also studied, and it was found that the selectivity ratio of aldehyde to alcohol could be varied by suitably changing the reaction conditions. This heterogeneous catalyst was found to give a 5-fold higher turnover number than the homogeneous cobalt–salen complex. [30]

A novel sulfonato-salen-nickel(II) complex has been immobilized on a Zn(II)-Al(III) layered double hydroxide (LDH) host. XRD, FT-IR, TGA and UV-vis spectroscopy, as well as chemical analysis, confirmed the successful incorporation of the nickel-salen complex within the LDH structure. BET surface area measurements, SEM and TEM were also used to characterize the heterogenized catalyst. The sulfonato-salen-nickel(II) complex-immobilized material, LDH-[nickel-salen], was found to be effective in the oxidation of tetralin, where a combination of trimethylacetaldehyde and dioxygen at atmospheric pressure was employed as the oxidant. At 72.3% conversion, tetralin was converted to 1-tetralone with 72.2% selectivity at 70 °C after 7 h. Tetralin oxidation using *tert*-butyl hydroperoxide afforded a lower conversion and selectivity of 1-tetralone than with trimethylacetaldehyde and dioxygen as the

oxidant. The effect of various reaction parameters on catalytic performance was also investigated. A hot filtration experiment coupled with a blank test revealed that oxidation proceeded mostly on nickel-salen sites in LDH-[nickel-salen]. A reaction mechanism is proposed based on the experimental results[31]

Layered double hydroxides (LDH) with brucite like structure was modified with various anionic surfactants containing sulfonate, carboxyl, phosphonate and sulfate end group through ion-exchange method. XRD reports indicated that the sulfonate group containing surfactants led to an adsorption process whereas the sulfate, carboxyl and phosphonate group containing surfactant led to an intercalation process. This can be evidenced from the change in basal spacing of LDH. The presence of anionic surfactants in the LDH was supported by FTIR spectroscopy. The FTIR spectrum indicated that complete removal of carbonate anion from the inter layer space of LDH is very difficult. The phosphonate intercalated HT showed less thermal stability than pristine LDH.[32]

A series of four chiral pentacoordinated aluminium salen complexes differing in the apical ligand have been prepared. The complexes exhibit an intense emission (λ from 0.271 to 0.35) arising from the LMCT band excitation. The complexes were submitted to laser flash photolysis. The same transient was observed in the four cases (τ under N₂ between 1.1 and 3.5 μ s) and the corresponding UV-visible transient spectrum exhibits two absorption bands at 320 and 500 nm. This transient is quenched by oxygen, hydrogen donors (1,4-cyclohexadiene and 1-octanethiol) and alkenes and it was assigned to the neutral Al salen complex generated by homolytic bond cleavage of the apical ligand. This transient exhibits different degrees of asymmetric recognition for its quenching with

enantiomerically pure pinene $kq(R)/kq(S)$ varying between 1.68 up to 12.26 depending on the nature of the apical ligand.[33]

1.4 Material Under Investigation

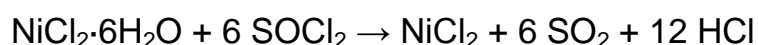
1.4.1 Nickel(II) chloride

Nickel(II) chloride (or just nickel chloride), is the chemical compound NiCl_2 . The anhydrous salt is yellow, but the more familiar hydrate $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is green. It is very rarely found in nature as mineral nickelbischofite. A dihydrate is also known. In general nickel(II) chloride, in various forms, is the most important source of nickel for chemical synthesis. Nickel salts are carcinogenic

1.4.1.1 Production and syntheses

Probably the largest scale production of nickel chloride involves the extraction with hydrochloric acid of nickel matte and residues obtained from roasting refining nickel-containing ores.

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is rarely prepared in the laboratory because it is inexpensive and has a long shelf-life. The hydrate can be converted to the anhydrous form upon heating in thionyl chloride or by heating under a stream of HCl gas. Simply heating the hydrates does not afford the anhydrous dichloride.



The dehydration is accompanied by a color change from green to yellow[34].

1.4.1.2 Structure and properties

NiCl_2 adopts the CdCl_2 structure[35]. In this motif, each Ni^{2+} center is coordinated to six Cl^- centers, and each chloride is bonded to three Ni(II) centers. In NiCl_2 the Ni-Cl bonds have “ionic character”. Yellow NiBr_2 and black NiI_2 adopt similar structures, but with a different packing of the halides, adopting the CdI_2 motif.

In contrast, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ consists of separated *trans*- $[\text{NiCl}_2(\text{H}_2\text{O})_4]$ molecules linked more weakly to adjacent water molecules. Note that only four of the six water molecules in the formula are bound to the nickel, and the remaining two are water of crystallisation[35]. Cobalt(II) chloride hexahydrate has a similar structure.

Many nickel(II) compounds are paramagnetic, due to the presence of two unpaired electrons on each metal center. Square planar nickel complexes are, however, diamagnetic.

1.4.1.3 Coordination chemistry

Most of the reactions ascribed to “nickel chloride” involve the hexahydrate, although specialized reactions require the anhydrous form.

Reactions starting from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ can be used to form a variety of nickel coordination complexes because the H_2O ligands are rapidly displaced by ammonia, amines, thioethers, thiolates, and organophosphines. In some derivative, the chloride remains within the coordination sphere, whereas chloride is displaced with highly basic ligands. Illustrative complexes include:

Coordinate geometry, colour and magnetizn of Different Salen crystal are shown in table 1.2 given below

Table 1.2 Coordinate geometry, colour and magnetizn of Different Salen

Crystal	Color	Magnetism	Geometry
$[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$	violet	paramagnetic	octahedral
$\text{NiCl}_2(\text{dppe})$	orange	diamagnetic	square planar
$[\text{Ni}(\text{CN})_4]^{2-}$	colorless	diamagnetic	square planar
$[\text{NiCl}_4]^{2-}$ [37,38]	Yellowish-Brown	paramagnetic	tetrahedral

Some nickel chloride complexes exist as an equilibrium mixture of two geometries; these examples are some of the most dramatic illustrations of structural isomerism for a given coordination number. For example, $\text{NiCl}_2(\text{PPh}_3)_2$, containing four-coordinate Ni(II), exists in solution as a mixture of both the diamagnetic square planar and the paramagnetic tetrahedral isomers. Square planar complexes of nickel can often form five-coordinate adducts.

NiCl_2 is the precursor to acetylacetonate complexes $\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2$ and the benzene-soluble $(\text{Ni}(\text{acac})_2)_3$, which is a precursor to $\text{Ni}(1,5\text{-cyclooctadiene})_2$, an important reagent in organonickel chemistry.

In the presence of water scavengers, hydrated nickel(II) chloride reacts with dimethoxyethane (dme) to form the molecular complex $\text{NiCl}_2(\text{dme})_2$. The dme ligands in this complex are labile. For

example, this complex reacts with sodium cyclopentadienide to give the sandwich compound nickelocene.

1.4.1.4 Properties

Nickel(II) chloride	
Identifiers	
CAS number	7718-54-9 , 7791-20-0 (hexahydrate)
PubChem	24385
EC number	231-743-0
RTECS number	QR6480000
Properties	
Molecular formula	NiCl ₂
Molar mass	129.5994 g/mol (anhydrous) 237.69 g/mol (hexahydrate)
Appearance	yellow-green crystals deliquescent
Density	3.55 g/cm ³ (anhydrous) 1.92 g/cm ³ (hexahydrate)
Melting point	1001 °C (anhydrous) 140 °C (hexahydrate)
Solubility in water	<i>anhydrous</i> 64 g/100 mL
	<i>hexahydrate</i> 254 g/100 mL (20 °C) 600 g/100 mL (100 °C)
Solubility in ethanol	Soluble (hexahydrate)
Structure	
Crystal structure	Monoclinic

Coordination geometry	octahedral at Ni
Thermochemistry	
Std enthalpy of formation $\Delta_f H_{298}^\circ$	-304.93 kJ/mol
Standard molar entropy S_{298}°	98.11 JK ⁻¹ mol ⁻¹
Hazards	
MSDS	Fischer Scientific
EU Index	028-011-00-6
EU classification	Carc. Cat. 1 Muta. Cat. 3 Repr. Cat. 2 Toxic (T) Irritant (Xi) Dangerous for the environment (N)
R-phrases	R49, R61, R23/25, R38, R42/43, R48/23, R68, R50/53
S-phrases	S53, S45, S60, S61
Flash point	Non-flammable
Related compounds	
Other anions	Nickel(II) fluoride Nickel(II) bromide Nickel(II) iodide
Other cations	Palladium(II) chloride Platinum(II) chloride Platinum(II,IV) chloride Platinum(IV) chloride
Related compounds	Cobalt(II) chloride Copper(II) chloride

1.4.1.5 Applications in organic synthesis

NiCl₂ and its hydrate are occasionally useful in organic synthesis[38]

- As a mild Lewis acid, e.g. for the regioselective isomerization of dienols:
- In combination with CrCl₂ for the coupling of an aldehyde and a vinylic iodide to give allylic alcohols.
- For selective reductions in the presence of LiAlH₄, e.g. for the conversion of alkenes to alkanes.
- As a precursor to “nickel boride”, prepared in situ from NiCl₂ and NaBH₄. This reagent behaves like Raney Nickel, comprising an efficient system for hydrogenation of unsaturated carbonyl compounds.
- As a precursor to finely divided Ni by reduction with Zn, for the reduction of aldehydes, alkenes, and nitro aromatic compounds. This reagent also promotes homo-coupling reactions, that is 2RX → R-R where R = aryl, vinyl.
- As a catalyst for making dialkyl arylphosphonates from phosphites and aryl iodide, ArI:



1.4.2 Copper(II) chloride

Copper(II) chloride is the chemical compound with the formula CuCl₂. This is a light green solid, much like neon green, which slowly absorbs moisture to form a blue-green dihydrate.

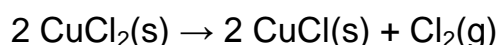
1.4.2.1 Structure

Anhydrous CuCl_2 adopts a distorted cadmium iodide structure. Most copper(II) compounds exhibit distortions from idealized octahedral geometry due to the Jahn-Teller effect, which in this case describes the localisation of one d-electron into a molecular orbital that is strongly antibonding with respect to a pair of ligands. In $\text{CuCl}_2(\text{H}_2\text{O})_2$ the copper can be described as a highly distorted octahedral complex, the Cu(II) center being surrounded by two water ligands and four chloride ligands, which bridge asymmetrically to other Cu centers[39].

1.4.2.2 Properties

Copper(II) chloride dissociates in aqueous solution to give the blue color of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and yellow or red color of the halide complexes of the formula $[\text{CuCl}_{2+x}]^x$. Concentrated solutions of CuCl_2 appear green because of the combination of these various chromophores. The color of the dilute solution depends on temperature, being green around 100 °C and blue at room temperature[40]. When copper(II) chloride is heated in a flame, it emits a green-blue colour. It is toxic and is only allowed in water in a concentration below 5ppm by the EPA.

It is a weak Lewis acid, and a mild oxidizing agent. It has a crystal structure consisting of polymeric chains of flat CuCl_4 units with opposite edges shared. It decomposes to CuCl and Cl_2 at 1000 °C:



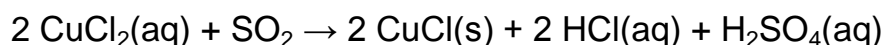
In its reaction with HCl (or other chloride sources) to form the complex ions CuCl_3^- and CuCl_4^{2-} [41].

Some of these complexes can be crystallized from aqueous solution, and they adopt a wide variety structural types .

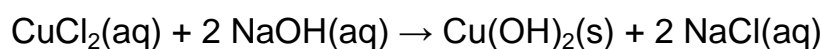
Copper(II) chloride also forms a rich variety of other coordination complexes with ligands such as pyridine or triphenylphosphine oxide:



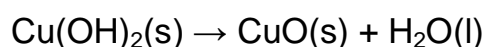
However "soft" ligands such as phosphines (e.g., triphenylphosphine), iodide, and cyanide as well as some tertiary amines cause reduction to give copper(I) complexes. To convert copper(II) chloride to copper(I) derivatives it is generally more convenient to reduce an aqueous solution with the reducing agent sulfur dioxide:



CuCl_2 can simply react as a source of Cu^{2+} in precipitation reactions for making insoluble copper(II) salts, for example copper(II) hydroxide, which can then decompose above 30 °C to give copper(II) oxide:



Followed by

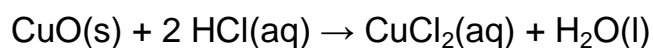


Copper(II) chloride	
Identifiers	
CAS number	7447-39-4 , 10125-13-0 (dihydrate)
PubChem	24014
RTECS number	GL7000000
Properties	
Molecular formula	CuCl ₂
Molar mass	134.45 g/mol (anhydrous) 170.48 g/mol (dihydrate)
Appearance	yellow-brown solid (anhydrous) blue-green solid (dihydrate)
Density	3.386 g/cm ³ (anhydrous) 2.51 g/cm ³ (dihydrate)
Melting point	498 °C (anhydrous) 100 °C (dehydration of dihydrate)
Boiling point	993 °C (anhydrous, decomp)
Solubility in water	70.6 g/100 mL (0 °C) 75.7 g/100 mL (25 °C)
Structure	
Crystal structure	distorted CdI ₂ structure
Coordination geometry	Octahedral
Hazards	
MSDS	Fischer Scientific
EU classification	Not listed
NFPA 704	0 2 1
Flash point	Non-flammable

Related compounds	
Other anions	Copper(II) fluoride Copper(II) bromide
Other cations	Copper(I) chloride Silver chloride Gold(III) chloride

1.4.2.3 Preparation

Copper(II) chloride is prepared by the action of hydrochloric acid on copper(II) oxide, copper(II) hydroxide or copper(II) carbonate, for example:



Anhydrous CuCl_2 may be prepared directly by union of the elements, copper and chlorine.

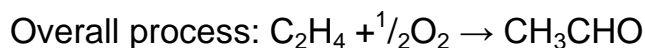
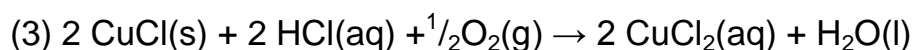
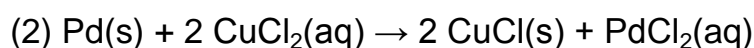
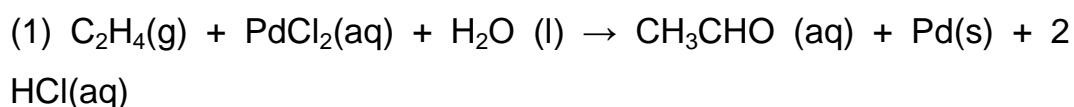
CuCl_2 may be purified by crystallisation from hot dilute hydrochloric acid, by cooling in a CaCl_2 -ice bath[42].

Electrolysis of aqueous sodium chloride with copper electrodes produces (among other things) CuCl_2 as a blue-green foam that can be skimmed off the top, collected, and dried to the hydrate.

Mixture of solutions of readily available copper II sulfate and sodium chloride yield a solution of copper II chloride. The sodium sulfate is an inert compound that does not generally enter any reaction.

1.4.2.4 Uses

A major industrial application for copper(II) chloride is as a co-catalyst (along with palladium(II) chloride) in the Wacker process. In this process, ethene (ethylene) is converted to ethanal (acetaldehyde) using water and air. In the process PdCl₂ is reduced to Pd, and the CuCl₂ serves to re-oxidise this back to PdCl₂. Air can then oxidise the resultant CuCl back to CuCl₂, completing the cycle.



Copper(II) chloride has a variety of applications in organic synthesis. It can effect chlorination of aromatic hydrocarbons- this is often performed in the presence of aluminium oxide. It is able to chlorinate the alpha position of carbonyl compounds[43].

This reaction is performed in a polar solvent such as DMF, often in the presence of lithium chloride, which speeds up the reaction rate.

CuCl₂, in the presence of oxygen, can also oxidise phenols. The major product can be directed to give either a quinone or a coupled product from oxidative dimerisation. The latter process provides a high-yield synthesis of 1,1-binaphthol (also called BINOL) and its derivatives, these can even be made as a single enantiomer in high enantiomeric excess[44].

Such compounds are valuable intermediates in the synthesis of BINAP and its derivatives, popular as chiral ligands for asymmetric hydrogenation catalysts.

Copper(II) chloride dihydrate is used for the hydrolysis of acetonides, i.e., for deprotection to regenerate diols[45] or aminoalcohols,[46] as in this example (where TBDPS = *tert*-butyldiphenylsilyl):

CuCl_2 also catalyses the free radical addition of sulfonyl chlorides to alkenes; the alpha-chlorosulfone may then undergo elimination with base to give a vinyl sulfone product.

Copper(II) chloride is also used in pyrotechnics as a blue/green coloring agent.

Copper chloride is also used as a root killer in landscaping and sewer line maintenance.

A voltaic cell may be made with a copper or brass electrode, copper II chloride, sodium chloride and zinc chloride-soaked papers, and a zinc electrode. These components must be stacked in the order given. It produces 0.84V at 150 milliamps.

1.4.5 Natural occurrence

Copper(II) chloride occurs naturally as the very rare mineral tolbachite and the dihydrate eriochalcite. Both are known from fumaroles. More common are mixed oxyhydroxide-chlorides like atacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$, arising among Cu ore beds oxidation zones in arid climate (also known from some altered slags).

References

- 1 Pfeiffer P., Breith E., Lübbe E., Tsumaki T. (1933). "Tricyclische orthokondensierte Nebervalenzringe".
- 2 Harvey Diehl, Clifford C. Hach (1950). "Bis(N,N' - Disalicylaethylenediamine) - μ - Aquodicobalt(II)
- 3 Tokuichi Tsumaki (1938). "Nebervalenzringverbindungen. IV. Über einige innerkomplexe Kobaltsalze der Oxyaldimine
- 4 Wu X., Gorden A. V. E.(2009). "2-Quinoxalinol Salen Copper Complexes for Oxidation of Aryl Methylenes".
- 5 Jay F. L. and Eric N. J. (2004), "(R,R)-N,N'-Bis(3,5-Di-tert-Butylsalicylidene)-1,2-Cyclohexanediamino Manganese(III) Chloride, A Highly Enantioselective Epoxidation Catalyst", *Org. Synth.*,
- 6 Thielert H., Pfeiffer P. (1938), *Chem. Ber.*, 71, 1399-1403.
- 7 Bailes R. H., Calvin M. (1947), *J. Am. Chem. Soc.*, 69, 1886-1893.
- 8 Czapinski J. L., Sheppard T. L. (2001), *J. Am. Chem. Soc.* , 123, 8618–8619.
- 9 Statistics generated by SciFinder Scholar(2006) upon searching for substructures of the basic salen ligand containing any metal.

- 10 Yoon T. P., Jacobsen E. N. (2003), *Science* , 299, 1691.
- 11 Zhang W., Loebach J. L., Wilson S. R., Jacobsen E. N.(1990), *J. Am. Chem. Soc.* 1990, 112, 2801.
- 12 Irie, R., Noda, K., Ito, Y., Matsumoto, N., Katsuki, T.(1990), *Tetrahedron Lett.*, 31, 7345.
- 13 McGarrigle E. M., Gilheany D. G. (2005), *Chem. Rev.*, 105, 1563-1602.
- 14 Katsuki T. (2002), *Adv. Synth. & Cat.*, 344, 131.
- 15 Katsuki T. (1995), *Coord. Chem. Rev.*, 140, 189.
- 16 Tokunaga M., Larrow J. F., Kakiuchi F., Jacobsen E. N. (1997), *Science* 1997, 277, 936.
- 17 Woollam J.A. and Somoano R.B. (1976) , *Phys. Rev.*, 13 3483
- 18 Rudorff W. and Sicks M.H. (1959), *Angew. Chem.*, 71 128.
- 19 Rudorff W. (1965), *Chimica*, 19 489
- 20 E. Bayer and W. Rudorff Z. (1959), *Naturforsch*, 71 128
- 21 Srivastava S.K., Avasthi B.N. and Mathur B.K. (1984), *J. Mat. Sci.Letts.*, 3 671-673

- 22 Leith R.M.A. (1977).(Ed.) Preparation and Crystal Growth of Materials with Layered Structures D (1977), Riedel Publication Company, Dordrecht Holland/Boston, U.S.A.
- 23 Nitsche R. (1960), J. Phys. Chem. Solids, 17 163
- 24 Nitsche R., Bolsterli H.U. and Lichtenstage M. (1961), J. Phys. Chem. Solids., 21 199
- 25 Brixner L.H. (1962), J. Inorg. Nucl. Chem., 24 257
- 26 Schafer H. (1964), Chemical Transport Reactions, Academic Press, New York.
- 27 Nitsche R. (1967), Crystal Growth, Ed. H.S. Peiser, Pergamon, Oxford, 215.
- 28 Nitsche R. (1966), Proceedings in International Conference on Crystal Growth (1966) Boston, J. Phys. Chem. Solids. Suppl., 1 ,215.
- 29 Kshirsagar V.S., Garade A.C., Mane R.B., Patil K.R., Yamaguchi A., Shirai M. and Rode C.V. Characterization of clay intercalated cobalt-salen catalysts for the oxidation of p-cresol
- 30 Chandrashekhar V. R., Vikas S. K., Jayprakash M. N. and Kashinath R. P. Cobalt–salen Intercalated Montmorillonite Catalyst for Air Oxidation of p-Cresol under Mild Conditions

- 31 Samiran B., Kwang-Eun J., Soon-Yong J. and Wha-Seung A., Synthesis of a sulfonato-salen-nickel(II) complex immobilized in LDH for tetralin oxidation
- 32 Anbarasan R., Lee W. D. And Im S. S., Adsorption and intercalation of anionic surfactants onto layered double hydroxides—XRD study
- 33 Carlos Baleizão, Bárbara Gigante, Fernando Ramôa Ribeiro, Belen Ferrer, Emilio Palomares c and Hermenegildo Garcia Photochemistry of chiral pentacoordinated Al salen complexes. Chiral recognition in the quenching of photogenerated tetracoordinated Al salen transient by alkenes
- 34 Pray A. P. (1990). "Anhydrous Metal Chlorides". *Inorganic Syntheses* 28: 321–2.
- 35 Wells A. F.(1984) *Structural Inorganic Chemistry*, Oxford Press, Oxford, United Kingdom.
- 36 Gill N. S. and Taylor F. B. (1967). "Tetrahalo Complexes of Dipositive Metals in the First Transition Series". *Inorganic Syntheses* 9: 136–142.
- 37 Stucky, J. B. (1967). "The Crystal and Molecular Structure of Tetraethylammonium Tetrachloronickelate(II)". *Acta Crystallographica* 23: 1064.

- 38 Tien-Yau L., Yu-Tsai H. (2001), "Nickel(II) Chloride" in *Encyclopedia of Reagents for Organic Synthesis* (L. A. Paquette, Ed.) J. Wiley & Sons, New York.
- 39 Wells A.F. (1984) *Structural Inorganic Chemistry*, Oxford: Clarendon Press.
- 40 Alfred S., Robert E. G., On P. (1848), in *Relation to Medical Jurisprudence and Medicine*. Lea & Blanchard, p. 378.
- 41 Simpson O.J. (1967). Tetrahalo Complexes of Dipositive Metals in the First Transition Series. *Inorg. Synth.* 9: 136–142.
- 42 Bertz S. H., Fairchild E. H. (1999), in *Handbook of Reagents for Organic Synthesis, Volume 1: Reagents, Auxiliaries and Catalysts for C-C Bond Formation*, (R. M. Coates, S. E. Denmark, eds.), pp. 220-3, Wiley, New York,.
- 43 Castro C. E., Gaughan E. J., Owsley D. C. (1965). Cupric Halide Halogenations. *Journal of Organic Chemistry* 30: 587.
- 44 Brussee J., Groenendijk J. L. G., Koppele J. M., Jansen A. C. A. (1985). On the mechanism of the formation of s(-)-(1, 1'-binaphthalene)-2,2'-diol via copper(II)amine complexes. *Tetrahedron* 41: 3313.

- 45 Chandrasekhar, M., Kusum L. C., and Vinod K. S. (2003). "Total Synthesis of (+)-Boronolide, (+)-Deacetylboronolide, and (+)-Dideacetylboronolide". *Journal of Organic Chemistry* 68 (10): 4039–4045.
- 46 Krishna, Palakodety R., Dayaker G. (2007). "A stereoselective total synthesis of (-)-andrachcinidine via an olefin cross-metathesis protocol". *Tetrahedron Letters* (Elsevier) 48: 7279–7282.
- 47 Pradyot P. (2002). *Handbook of Inorganic Chemicals*. McGraw-Hill,
- 48 Holleman A.F., Wiberg E. (2001). *Inorganic Chemistry*. San Diego: Academic Press.
- 49 Tarr B.R. (1950). Anhydrous Iron(III) Chloride. *Inorganic Syntheses* 3: 191–194.
- 50 Pray A. R., Richard F. H., Stanley S. (1990). Anhydrous Metal Chlorides. *Inorganic Syntheses* 28: 321–323.
- 51 (PDF) *Water Treatment Chemicals*. Akzo Nobel Base Chemicals. 2007.
- 52 *Separation and Purification Technology* 51 (2006) pp 332-337
- 53 *Chem. Eng. Sci.* 61 (2006) pp 229-245
- 54 Greenwood N.N., Earnshaw A. (1997). *Chemistry of the*

Elements (2nd ed.). Oxford: Butterworth-Heinemann

- 55 Furnell B.S.(1989). *Vogel's Textbook of Practical Organic Chemistry* (5th ed.). New York: Longman/Wiley.
- 56 Kealy T.J. (1951). A New Type of Organo-Iron ompound.
Nature 168: 1040.
- 57 Kamal A. (2002). "Mild and efficient reduction of azides to amines: synthesis of fused [2,1-*b*]quinazolines. *Tetrahedron Letters* 43: 6961.
- 58 Tseng M. (2006). Transendothelial migration of ferric ion in FeCl₃ injured murine common carotid artery. *Thrombosis Research* 118: 275–280.