

# [Understanding the chemistry of nickel](https://assignbuster.com/understanding-the-chemistry-of-nickel/)

Nickel is silvery white [1] and lustrous metal. It is the 7th most abundant transition metal and 24th most abundant element in the crust of earth. It has an atomic number of 28, atomic mass of 58. 71 gmol-1 and atomic volume of 6. 59 cm3mol-1 [2]. It belongs to group 10 (8B) and 4th period of modern periodic table. Nickel has electronic configuration [Ar] 4s2 3d8 [3]. It has property of malleability and ductility. 300 kilometers long wire can be drawn from a single kilogram of nickel. It has high electrical and thermal conductivities of 0. 146 x 106 Scm-1 and 90. 9 Wm-1K-1. It is hard, odorless and corrosion resistant metal that takes a high polish.

Nickel crystallizes with face centered cubic structure. The unit cell has lattice parameter of 0. 352 nm with atomic radius of 0. 124 nm. Nickel is naturally occuring ferro magnetic and magnetostrictive material [4] at or near room temperature. Its curie temperature is 355 °C [5].

Nickel is mined from two types of ore deposits. These include laterites and sulphides. Laterites are silicate or oxide ores. It occurs most usually in combination with sulfur and iron in pentlandite (NiS. 2FeS) which contains 1. 5% nickel, with sulfur in millerite (NiS), with arsenic in mineral nickeline (NiAs) as a red nickel ore, containing 43. 9% nickel and 56. 1% arsenic, and with arsenic and sulfur in nickel glance [6].

## 1. 2 Chemical Properties of Nickel

Nickel is relatively unreactive element. Under ambient conditions, it does not react with water, oxygen or dissolve in most acids.

## 1. 2. 1 Standard Reduction Potentials

In aqueous solution, the standard reduction potentials for various oxidation states of nickel are shown in Scheme 1. 1 [7, 8].

## Scheme 1. 1 Standard Electrode Potentials of Various Nickel Species

## 1. 2. 2 Reaction of Nickel with Halogens

Nickel dichloride, NiCl2, nickel dibromide, NiBr2, and nickel diiodide, NiI2, are formed by the reactions of nickel with chlorine, Cl2, bromine, Br2, and iodine, I2.

Ni(s) + Cl2(g) â†’ NiCl2(s) (yellow)

Ni(s) + Br2(g) â†’ NiBr2(s) (yellow)

Ni(s) + I2(g) â†’ NiI2(s) (black)

## 1. 2. 3 Reaction of Nickel with Acids

Nickel metal dissolves slowly in dilute sulphuric acid to form solution containing the aquated Ni(II) ion together with hydrogen gas, H2.

Ni(s) + H2SO4(aq) â†’ Ni2+(aq) + SO42-(aq) + H2(g)

Ni(s) + HCl(aq) â†’ Ni2+(aq) + Cl- (aq) + H2(g)

It does not dissolve in concentrated nitric acid, HNO3, because it is rendered passive by this reagent [9].

## 1. 2. 4 Reaction of Nickel with Air

Nickel in finely divided form reacts readily with air. At higher temperatures, it burns in oxygen to form nickel oxide.

2Ni(s) + O2(g) â†’ 2NiO(s)

## 1. 3 Oxidation States

The oxidation states of nickel include -1, 0, +1, +2, +3 or +4. The most prevalent oxidation state is +2, but compounds of Ni0, Ni+1, and Ni3+ are well known. Ni4+ has also been demonstrated [10].

## 1. 4 Nickel(II) Compounds

Nickel is known primarily for its divalent compounds with all common anions, i. e. halides, hydroxide, sulfate, carbonate, carboxylates, sulfide and hydroxide. Green and blue are the characteristic colors of its compounds. Important nickel(II) compounds include:

## 1. 4. 1 Oxides

Nickel oxide, NiO is a powdery green solid that becomes yellow on heating [11]. It can be prepared easily by heating nickel carbonate, nitrate or hydroxide.

## 1. 4. 2 Sulfides

Nickel sulfides occur in different forms such as NiS, nickel sulphide, NiS2, nickel persulphide and Ni3S2, trinickel disulphide.

## 1. 4. 3 Halides

NiCl2 is yellow but NiCl2. 6H2O is of green colour. NiCl2 is prepared by

NiCl2. 6H2O + 6SOCl2 â†’ NiCl2 + 6SO2 + 12HCl

NiF2 is prepared by treatment of anhydrous nickel(II) chlHYPERLINK “ http://en. wikipedia. org/wiki/Nickel(II)\_chloride” oride with fluorine at 350 °C [12].

NiClHYPERLINK “ http://en. wikipedia. org/wiki/Nickel(II)\_chloride” 2 + FHYPERLINK “ http://en. wikipedia. org/wiki/Fluorine” 2 â†’ NiF2 + ClHYPERLINK “ http://en. wikipedia. org/wiki/Chlorine” 2

## 1. 4. 4 Nitrates

Nickel(II) nitrate hexahydrate, Ni(NO3)2. 6H2O is highly soluble in water, giving emerald green solutions.

## 1. 4. 5 Carbonates

Nickel(II) carbonate is a pale green polymeric solid consisting of Ni2+ cations and [COHYPERLINK “ http://en. wikipedia. org/wiki/Carbonate” 3HYPERLINK “ http://en. wikipedia. org/wiki/Carbonate”]HYPERLINK “ http://en. wikipedia. org/wiki/Carbonate” 2- anions. It is readily decomposed by aqueous acids to give solutions containing the ion [Ni(H2O)6]2+, liberating water and carbon dioxide.

## 1. 4. 6 Sulfates

The anhydrous form has a yellow to green color while NiSO4. 7H2O and NiSO4. 6H2O appears green and blue to pale green, respectively.

## 1. 4. 7 Hydroxides

Ni(OH)2 occurs as green crystals that can be precipitated when aqueous alkali is added to a solution of nickel (II) salt. Its decomposition on heating above 230 °C produces toxic gases.

## 1. 5 Nickel (III), Nickel (IV) & Nickel (VI) Compounds

The +3 oxidation state is found in dinickel trioxide, Ni2O3. NiO4-2 is an example of +6 oxidation state while NiO2 and NiF6-2 correspond to +4 oxidation states. Nickel(IV) also occurs in BaNiO3 and in the periodate salts, MNiIO6 (M = alkali cation, NH4).

## 1. 6 Water Soluble, Poorly Soluble & Insoluble Nickel

## Compounds

In contrast to water soluble nickel salts (chloride, nitrate, acetate and sulfate), metallic nickel, nickel sulfides, and nickel oxides are poorly soluble in water [13]. NiCO3 is partly water soluble.

## 1. 7 Nickel(II) Complexes

Nickel in its most common +2 oxidation state displays a wider range of geometries in its complexes than any other metal ion with coordination numbers 3 to 6.

Nickel(II) forms many complexes with octahedral [14, 15], square planar [16, 17, 18] and tetrahedral [19, 20] geometries and a smaller number of five coordinate compounds [21, 22] with square pyramidal and trigonal bipyramidal arrangements. Nickel(II) octahedral, trigonal bipyramidal, square pyramidal and tetrahedral complexes are paramagnetic and have in the majority of cases a green or blue colour. The square planar nickel complexes are diamagnetic and mostly have a yellow, red or brown colour.

The ligand exchange processes for nickel(II) tend to be associative, while with palladium(II) and platinum(II), dissociative pathways predominate which tends to adopt only square planar complexes.

## 1. 7. 1 Six Coordinate Octahedral Nickel(II) Complexes

Nickel(II) forms octahedral complexes with neutral ligands such as H2O and NH3. Amines displace some or all of water molecules in the octahedral [Ni(H2O)6]2+ ion to form complexes such as trans [Ni(H2O)2(NH3)4]2+, [Ni(NH3)6]2+ and [Ni(en)3]2+. These complexes are characteristically purple or blue in contrast to the bright green hexaaquanickel(II) ion, [Ni(H2O)6]2+ [23].

These octahedral complexes have two unpaired electrons and are paramagnetic with magnetic moments 2. 9 to 3. 4 BM. Other examples include dichlorobis(ethylenediamine)nickel(II), a blue solid, soluble in water and polar organic solvents [24] and Ni(acac)2. 2H2O [25].

## 2+ 2+

## [Ni(H2O)6]2+ [Ni(NH3)6]2+

## Ni(en)2Cl2 Ni(acac)2. 2H2O

## 1. 7. 2 Five Coordinate Square Pyramidal & Trigonal Bipyramidal

## Nickel(II) Complexes

Several phosphine and arsine ligands form five coordinate trigonal bipyramidal complexes because tetradentate “ tripod” ligands such as N[C2H4N(CH3)2]3 and N[C2H4PPh2]3 cannot span the apices of a regular tetrahedron. One face is left open for 5th ligand, e. g halide ion to form trigonal bipyramidal complex. Though hydride, thiolate, alkyl and other anionic ligands are also known; the complexes are therefore +1 cations.

Tris(1, 3-diaminopropane) chromium(III) pentacyanonickelate(II), [Cr(tn)3][Ni(CN)5] has square pyramidal [Ni(CN)5]3- anions. In contrast, crystalline tris(ethylenediamine) chromium(III) pentacyanonickelate(II) sesquihydrate, [Cr(en)3][Ni(CN)5]. 1. 5H2O contains both square pyramidal anions and slightly distorted trigonal bipyramidal anions [26].

## The trigonal bipyramidal structure is favored on the basis of ligand repulsion alone. For this reason, almost every five coordinate compound having non metallic central element such as PF5 has trigonal bipyramidal structure unless there are lone pairs.

## 1. 7. 3 Four Coordinate Nickel(II) Complexes

Nickel(II) in its four coordination mode exhibits either tetrahedral or square planar geometry.

## 1. 7. 3. 1 Tetrahedral Nickel(II) Complexes

Nickel(II) tetrahedral complexes of stoichiometric types; NiX42-, NiX3L-, NiL2X2 and Ni(L-L)2 are known where X represents halogen, L is neutral ligand such as phosphine, phosphine oxide or arsine, and L-L is bidentate ligand such as ethylenediamine. Tetrahedral arrangement for Ni2+ will be preferred if the ligands are large and weak field.

## Ni(PPh3)3Cl NiCl42-

## [Ni(acac)2]

## 1. 7. 3. 2 Square Planar Nickel(II) Complexes

For the vast majority of four coordinate nickel(II) complexes, planar geometry is preferred for small and strong field ligands. Tetracyanonickelate(II) will probably be orange red colored square planar complex. Almost all planar complexes of nickel(II) with d8 configuration are diamagnetic. Important examples of square planar complexes are red bis(dimethylglyoximato) nickel(II) [27] and dichloro[1, 3-bis(diphenylphosphino)propane]nickel, NiCl2(dppp).

Ni(dmgH)2 NiCl2(dppp)

[Ni(C2O4)2]2- [Ni(CN)4]2-

## 1. 7. 4 Three Coordinate Nickel(II) Complexes

There are many examples of trigonal complexes for nickel(0), however, they are rare for Ni(II). The examples include dialkylamides [Ni(NR2)3]1- and Ni2( µ-NR2)2(NR2)2 as well as blue mesityl complex [Ni(mes)3]1- which has approximately T – shaped geometry [28, 29].

## 1. 8 Nickel(III) Complexes

[Ni(tdt)2]- is nickel(III) square planar complex anion having coordination number four where tdt = 3, 4-toluenedithiole. Other examples include [Ni(tacn)2]3+ with 1, 4, 7-triazacyclononane [30] and dark green air stable Ni(III) complex having donor NO2S2 chromophore [31].

## Ni[(NO2S)2(C6H4)4] [Me(tdt)2]-, Me = Ni

## [Ni(tacn)2]3+

## 1. 9 Nickel(IV) Complexes

A well established bis chelated complex of nickel(IV) is the diacetylpyridine dioximato complex [32]. Other examples include dicarbollide complex, Ni(closo-1, 2-C2B9H11)2 [33] and the polyselenide anion [Ni4Se4(Se3)(Se4)]4- with a cubic Ni4Se4 core [34]. The hexadentate ligand 3, 14-dimethyl-4, 7, 10, 13-tetraazahexadeca-3, 13-diene 2, 15-dione dioxime forms pseudooctahedral NiN6 complex with nickel(IV) [35].

## 1. 10 Nickel(-I, 0, +I) Complexes

The low valent oxides, K3[NiO2] and KNa2[NiO2] contain linear [O-Ni(I)-O]3- units [36]. The majority of nickel(I) complexes contain phosphine ligands and have tetrahedral or trigonal bipyramidal structure. They are paramagnetic as expected for d9 configurations. In Ni(CO)4, nickel is in zero oxidation state [37]. Bis(cyclooctadiene)nickel(0), Ni(C8H12)2 is a diamagnetic featuring tetrahedral nickel(0) [38].

## Ni(cod)2 Ni(CO)4

## 1. 11 Biological Role

Nickel is a part of urease. [NiFe]-hydrogenases selectively oxidise H2. Carbon monoxide dehydrogenase enzymes consists of Fe-Ni-S cluster [39]. Other nickel containing enzymes include class of superoxide dismutase and glyoxalase [40].

Enzymatic reactions depend on redox activity of nickel atoms in enzyme’s active site. In fact, proposed mechanisms of NiFe hydrogenase [41], methyl-CoM reductase [42, 43] and NiSOD [44, 45] involves reduced (Nio, Ni+) and or oxidized (Ni3+) forms of nickel. Nickel along with iron plays vital role in transport of oxygen in blood. Nickel also acts as co-factor in absorption of iron from intestine.

## 1. 12 Sources and Potential Exposure of Nickel

Nickel is a ubiquitous natural trace element and it occurs in air, water and soil of the biosphere [46].

## 1. 12. 1 Diet

Food and drinking water [47, 48] are the major sources of nickel exposure [49]. Fats, chocolates [50], nuts, candies [51], tomatoes, bananas, onions, spinach, legumes, tea [52], white flour and all canned foods [53] are rich in nickel content.

## 1. 12. 2 Ambient Air

Nickel oxide, nickel chloride, nickel carbonyl and nickel subsulphide are inhaled pollutants. Nickel levels in ambient air are in range 1 – 10 ng/m3 in urban areas, although much higher levels 110 – 180 ng/m3 have been recorded in heavily industrialized areas and larger cities [54].

## 1. 12. 3 Tobacco Smoking

It is major source of nickel in indoor air. A cigarette contains 1 – 3 µg of nickel. Nickel in a burning cigarette form nickel tetracarbonyl that is volatile and gaseous compound and badly affects respiratory tract [55].

## 1. 12. 4 Occupational Exposure of Nickel

Pulmonary absorption is major route of nickel exposure in industries [56]. The general population is also exposed to nickel in nickel alloys and nickel plated materials such as coins [57], jewellery [58], electric guitar strings [59], stainless steel cutlery, soaps and detergents.

## 1. 13 Exposure Limits of Nickel

The American Conference of Governmental and Industrial Hygienists (ACGIH) has assigned threshold limit value time weighted average for exposure to nickel compounds is 1. 5 mg/m3 for elemental nickel, 0. 1 mg/m3 for soluble inorganic nickel compounds and nickel subsulfide, 0. 2 mg/m3 for insoluble inorganic compounds and 0. 05 ppm for nickel carbonyl [60].

## 1. 14 Toxicity of Nickel

Nickel is known as haemato, immunoto, neuro, geno, reproductive, pulmonary toxic and carcinogenic agent.

## 1. 14. 1 Acute Toxicity (01 day)

The accidental inhalation of nickel carbonyl causes acute toxic effects in two stages, immediate and delayed. The immediate symptoms include headache, vertigo, irritability, which usually last a few hours, followed by an asymptomatic interval of 12 h to 5 days. The delayed symptoms are:

## 1. 14. 1. 1 Nickel Itch

Soluble nickel compounds on skin contact may result in “ nickel itch” [61], most frequently when skin is moist.

## 1. 14. 1. 2 Gastrointestinal Distress

Nausea, vomiting and diarrhea were reported in workers who drank water, contaminated with nickel sulfate and nickel chloride.

## 1. 14. 1. 3 Neurological Effects

Giddiness and weariness were reported in individuals accidentally exposed to nickel sulphate and nickel chloride (1. 63 g Ni/liter) with boric acid in drinking water [62].

## 1. 14. 1. 4 Pulmonary Fibrosis

In humans and animals, nickel carbonyl causes pulmonary fibrosis. Nickel fumes are respiratory irritants and may also cause pneumonitis.

## 1. 14. 1. 5 Kidney Damage

Kidney damage and frank haematuria were observed [63].

## 1. 14. 2 Subchronic Toxicity (10 – 100 day)

A 6 weeks exposure of nickel fumes (0. 07 – 1. 1 mg nickel/m3) in humans caused an increase in air way and eye irritations, headaches and tiredness [64].

## 1. 14. 3 Chronic Toxicity (> 100 days)

## 1. 14. 3. 1 Dermatitis

In sensitized individuals, it is most common effect due to nickel use in jewellery intended for pierced body parts and is often marked by itchy and red skin followed by skin ulceration [65].

## 1. 14. 3. 2 Respiratory Disorders

Inhalation of nickel dusts and aerosols contributes to respiratory disorders such as asthma [66], pneumoconiosis and can also interfere with kreb´s cycle.

## 1. 14. 3. 3 Heart Failure

Exposure of nickel tetracarbonyl to levels 50, 000 – 100, 000 times greater than levels normally encountered in food or drinking water can cause heart failure and variable degrees of cardiovascular system poisoning [67].

## 1. 14. 3. 4 Tumors

Nickel powder can induce both epithelial and connective tissue tumors e. g. pelvic, renal cortical and liver tumors when given by subcutaneous, intramuscular or intraperitoneal injection [68].

## 1. 14. 3. 5 Kidney Poisoning

Nickel in blood is mostly protein bound and accumulates primarily in kidneys resulting in kidney poisoning [69].

## 1. 14. 3. 6 Birth Defects

Low birth weight infants with sensory abnormalities, such as hearing or sight loss and cardiac malformations are born with nickel exposed mothers [70, 71].

## 1. 14. 3. 7 Oxidative Stress

Nickel(II) induces oxidative stress in humans [72, 73] by producing either reactive oxygen species, ROS or reactive nitrogen species, RNS. NiCl2 induces lipid peroxidation while ROS generated damage DNA. Nickel binds to DNA repair enzymes and generates oxygen free radicals causing protein degradation [74].

## 1. 14. 3. 8 Genotoxicity

Ni(CO)4 inhibts DNA dependent RNA synthesis activity by binding to chromatin or DNA and thereby preventing action of RNA polymerase, causing suppresion of messenger RNA dependent induction of enzyme synthesis [75].

## 1. 14. 3. 9 Carcinogenicity

Nickel subsulphide, nickel oxide, nickel sulphate as well as nickel sulfide fume and dust is believed to be carcinogenic [76, 77]. Independent international scientific bodies have classified mixed sulphidic and oxidic nickel compounds [78] as carcinogens to humans, inclusive of water soluble nickel compounds. There are higher chances of development of lung cancer, nasal cancer, and Prostate cancer in nickel exposed workers [79].

## 1. 15 Uses of Nickel

## 1. 15. 1 Nickel Alloys

Nickel in alloyed form has made significant contributions to our present day society. German silver containing 10 – 30 % nickel is used for ornamental and domestic objects. Monel contains 68% nickel ands is used in apparatus for handling corrosive materials. Invar is important due to very small coefficient of expansion [80].

Nickel is principle alloying element in stainless steel that enhances its heat, corrosion, and stress rupture resistance [81]. Majority of stainless steels contain 8 – 10 % nickel. Its limitless uses include home and industrial products.

## 1. 15. 2 Nickel Electroplating

Nickel electroplating is used for both protective and decorative finishes. Nickel chloride, NiCl2, nickel acetate Ni(OCOCH3)2, nickel nitrate, Ni(NO3)2. 6H2O and nickel sulphate, NiSO4. 7H2O are employed chiefly in nickel electroplating baths [82] while nickel oxide is used as electrolyte. Nickel electroplating changes the chemical, physical and mechanical properties of the workpiece [83].

## 1. 15. 3 Catalytic Hydrogenation

Raney nickel is used in a large number of industrial processes because of its stability and high catalytic activity at room temperature. It catalyses hydrogenation of vegetable oils. Soybean oil has been hydrogenated electrocatalytically on raney nickel with 90 – 100 % efficiencies [84].

Benzene is commonly reduced to cyclohexane using raney nickel for production of nylon.

## Reduction of Benzene to Cyclohexane Using Raney Nickel

Raney nickel is used in reduction of compounds that have multiple bonds.

## Reduction of Thiophene by Raney Nickel

## De-Sulfurization of Thioacetals using Raney Nickel

## 1. 15. 4 Industrial Applications of Nickel

## 1. 15. 4. 1 Heavy Industries

Nickel based super alloys have high temperature applications in jet engines, gas turbines and rocket engines [85]. Monel can resist corrosion by sea water and is ideal for propeller shaft in boats and desalination plants.

## 1. 15. 4. 2 Food & Chemical processing Industries

Monel and stainless steel are used in chemical and food processing industries due to better corrosion resistance at high temperature steam [86].

## 1. 15. 4. 3 Ceramics, Paints, Dyes & Cosmetic Industries

Nickel(II) phthalocyanine, C32H16N8Ni is used as bluish green pigment in the coloring industries [87]. The nickel titanium yellow pigments find great use in polymer and paint applications [88].

Nickel dimethylglyoxime (C8 H14 N4 NiO4) is routinely used as coloring agent in paints, cosmetics and certain kinds of plastics. NiO is used in making glass having ability to absorb visible light but transmits ultraviolet light [89]. In cosmetic products of many brands, the highest level of nickel in eye shadows is about 49 ppm [90].

## 1. 15. 4. 4 Textile & Rubber Industry

Nickel acetate is used as mordant in textile industry. Di-n-butyldithiocarbamate nickel(II) complex, Ni[CS2N(C4H4)2]2 is used as an antioxidant in tires.

## 1. 15. 5 Batteries

Nickel batteries are dominant in the field of rechargeable electrochemical power sources due to their long cycle life, high power and a reliable performance. Ni(OH)2 is used as positive electrode to significantly boost energy densities in nickel alkaline batteries [91]. Nickel cadmium cells provide 1. 2 V and are used in aeroplanes and emergency lighting systems. In industries, these batteries provide high voltage of 250 V with capacities about 5 Ah – 100 Ah [92].

Nickel hydrogen (NiH2) battery cells with nickel oxide positive electrode are developed due to high power density and good thermal performance which make them attractive for use in electric vehicles, satellite and space power systems [93].

## 1. 16 Chemistry of Ligands

## 1. 16. 1 Thiourea (Tu)

Thiourea, SHYPERLINK “ http://en. wikipedia. org/wiki/Carbon” C(NHYPERLINK “ http://en. wikipedia. org/wiki/Hydrogen” H2)2 is lustrous white crystalline compound. It is useful sulfur donor thioamide and planar molecule, soluble in water and polar organic solvents but insoluble in non polar solvents.

## It has two tautomeric forms but in aqueous solution, thione form predominates.

## 1. 16. 2 N, N’-Dimethylthiourea (Dmtu)

N, N’-Dimethylthiourea, C3H8N2S has appearance of colorless to white crystals. It shows coordination through sulfur.

## Fig. 1. 10 Structure of N, N’-Dimethylthiourea

## 1. 16. 3 1, 1, 3, 3-Tetramethyl-2-thiourea (Tmtu)

This substituted thiourea is white crystalline solid. It is sulfur donor ligand.

## 1. 16. 4 1, 3-Diazinane-2-thione (Diaz)

This six membered heterocyclic thione is sulfur donor ligand.

## 1. 16. 5 Imidazolidine-2-thione (Imt)

It is a sulfur donor five membered heterocyclic thione [94] and has brown crystals. The peculiarity of Imidazolidine-2-thione is presence of a thiouredine fragment. It is planar with non-uniform distribution of Ï€ electron density and shows presence of maximum negative charge on exocyclic sulfur.

## Dipolar form B predominates in resonance hybrid.

## 1. 17 Objective

The primary objective of this study is to understand basic chemistry of nickel(II) and its complexes and gain an insight into metal ligand interactions in biological systems with following main objectives.

To explore coordination chemistry of nickel(II) with various sulfur donor ligands and develop useful model for biologically active nickel complexes by determining structures of synthesized nickel complexes.

Synthesis of nickel(II) complexes with thioamide and thione ligands.

Crystallization of as many complexes as possible and determination of their structures by X-ray crystallography.

Characterization of complexes by IR and UV-VIS spectroscopy.

A comparative study of complexes based on spectroscopic and structural data.