

# Understanding the chemistry of nickel



**ASSIGN  
BUSTER**

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 g mol<sup>-1</sup> and atomic volume of 6.59 cm<sup>3</sup> mol<sup>-1</sup> [2]. It belongs to group 10 (8B) and 4th period of modern periodic table. Nickel has electronic configuration [Ar] 4s<sup>2</sup> 3d<sup>8</sup> [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  $0.146 \times 10^6$  S cm<sup>-1</sup> and 90.9 W m<sup>-1</sup> K<sup>-1</sup>. 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 occurring 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.

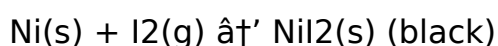
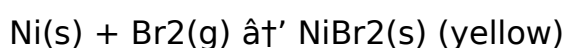
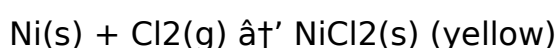
## 1. 2. 1 Standard Reduction Potentials

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

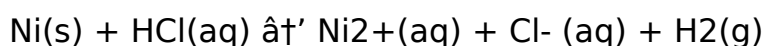
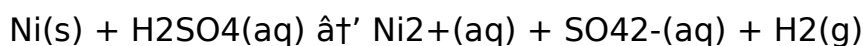
## 1. 2. 2 Reaction of Nickel with Halogens

Nickel dichloride, NiCl<sub>2</sub>, nickel dibromide, NiBr<sub>2</sub>, and nickel diiodide, NiI<sub>2</sub>, are formed by the reactions of nickel with chlorine, Cl<sub>2</sub>, bromine, Br<sub>2</sub>, and iodine, I<sub>2</sub>.



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

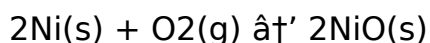
Nickel metal dissolves slowly in dilute sulphuric acid to form solution containing the aquated Ni(II) ion together with hydrogen gas, H<sub>2</sub>.



It does not dissolve in concentrated nitric acid, HNO<sub>3</sub>, 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.



## 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 Ni<sup>0</sup>, Ni<sup>+1</sup>, and Ni<sup>+3</sup> are well known. Ni<sup>+4</sup> 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

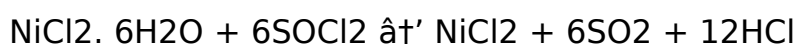
Nickel oxide, NiO is a powdery green solid that becomes yellow on heating [11]. It can be prepared easily by heating nickel carbonate, nitrate or hydroxide.

### 1. 4. 2 Sulfides

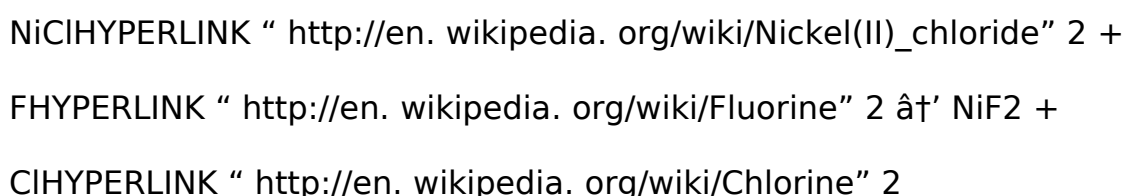
Nickel sulfides occur in different forms such as NiS, nickel sulphide, NiS<sub>2</sub>, nickel persulphide and Ni<sub>3</sub>S<sub>2</sub>, trinickel disulphide.

### 1. 4. 3 Halides

NiCl<sub>2</sub> is yellow but NiCl<sub>2</sub> · 6H<sub>2</sub>O is of green colour. NiCl<sub>2</sub> is prepared by



NiF<sub>2</sub> is prepared by treatment of anhydrous nickel(II) chloride with fluorine at 350 °C [12].



### 1. 4. 4 Nitrates

Nickel(II) nitrate hexahydrate, Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O is highly soluble in water, giving emerald green solutions.

### 1. 4. 5 Carbonates

Nickel(II) carbonate is a pale green polymeric solid consisting of Ni<sup>2+</sup> cations and [CO<sub>3</sub>]<sup>2-</sup> anions. It is readily decomposed by aqueous acids to give solutions containing the ion [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, liberating water and carbon dioxide.

### 1. 4. 6 Sulfates

The anhydrous form has a yellow to green color while NiSO<sub>4</sub> · 7H<sub>2</sub>O and NiSO<sub>4</sub> · 6H<sub>2</sub>O appears green and blue to pale green, respectively.

### **1. 4. 7 Hydroxides**

$\text{Ni(OH)}_2$  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  $230\text{ }^\circ\text{C}$  produces toxic gases.

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

The +3 oxidation state is found in dinickel trioxide,  $\text{Ni}_2\text{O}_3$ .  $\text{NiO}_4^{2-}$  is an example of +6 oxidation state while  $\text{NiO}_2$  and  $\text{NiF}_6^{2-}$  correspond to +4 oxidation states. Nickel(IV) also occurs in  $\text{BaNiO}_3$  and in the periodate salts,  $\text{MNiO}_6$  (M = alkali cation,  $\text{NH}_4$ ).

### **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].  $\text{NiCO}_3$  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 H<sub>2</sub>O and NH<sub>3</sub>. Amines displace some or all of water molecules in the octahedral [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> ion to form complexes such as trans [Ni(H<sub>2</sub>O)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> and [Ni(en)<sub>3</sub>]<sup>2+</sup>. These complexes are characteristically purple or blue in contrast to the bright green hexaaquanickel(II) ion, [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> [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)<sub>2</sub> · 2H<sub>2</sub>O [25].

$2+ 2+$

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+} [\text{Ni}(\text{NH}_3)_6]^{2+}$

$\text{Ni}(\text{en})_2\text{Cl}_2 \text{Ni}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$

## 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  $\text{N}[\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2]_3$  and  $\text{N}[\text{C}_2\text{H}_4\text{PPh}_2]_3$  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),  $[\text{Cr}(\text{tn})_3][\text{Ni}(\text{CN})_5]$  has square pyramidal  $[\text{Ni}(\text{CN})_5]^{3-}$  anions. In contrast, crystalline tris(ethylenediamine) chromium(III) pentacyanonickelate(II) sesquihydrate,  $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5] \cdot 1.5\text{H}_2\text{O}$  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  $\text{PF}_5$  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

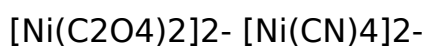
Nickel(II) tetrahedral complexes of stoichiometric types;  $NiX_4^{2-}$ ,  $NiX_3L^-$ ,  $NiL_2X_2$  and  $Ni(L-L)_2$  are known where X represents halogen, L is neutral ligand such as phosphine, phosphine oxide or arsine, and L-L is bidentate ligand such as ethylenediamine. Tetrahedral arrangement for  $Ni^{2+}$  will be preferred if the ligands are large and weak field.



### 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(dimethylglyoximate) nickel(II) [27] and dichloro[1, 3-bis(diphenylphosphino)propane]nickel,  $NiCl_2(dppp)$ .



### 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  $[Ni(NR_2)_3]^{1-}$  and  $Ni_2(\mu-NR_2)_2(NR_2)_2$  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)<sub>2</sub>]<sup>-</sup> is nickel(III) square planar complex anion having coordination number four where tdt = 3, 4-toluenedithiole. Other examples include [Ni(tacn)<sub>2</sub>]<sup>3+</sup> with 1, 4, 7-triazacyclononane [30] and dark green air stable Ni(III) complex having donor NO<sub>2</sub>S<sub>2</sub> chromophore [31].



## 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-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub> [33] and the polyselenide anion [Ni<sub>4</sub>Se<sub>4</sub>(Se<sub>3</sub>)(Se<sub>4</sub>)<sub>4</sub>]<sup>-</sup> with a cubic Ni<sub>4</sub>Se<sub>4</sub> core [34]. The hexadentate ligand 3, 14-dimethyl-4, 7, 10, 13-tetraazahexadeca-3, 13-diene 2, 15-dione dioxime forms pseudooctahedral NiN<sub>6</sub> complex with nickel(IV) [35].

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

The low valent oxides, K<sub>3</sub>[NiO<sub>2</sub>] and KNa<sub>2</sub>[NiO<sub>2</sub>] contain linear [O-Ni(I)-O]<sub>3</sub><sup>-</sup> units [36]. The majority of nickel(I) complexes contain phosphine ligands and have tetrahedral or trigonal bipyramidal structure. They are paramagnetic as expected for d<sup>9</sup> configurations. In Ni(CO)<sub>4</sub>, nickel is in zero oxidation state [37]. Bis(cyclooctadiene)nickel(0), Ni(C<sub>8</sub>H<sub>12</sub>)<sub>2</sub> is a diamagnetic featuring tetrahedral nickel(0) [38].

## **Ni(cod)<sub>2</sub> Ni(CO)<sub>4</sub>**

### **1. 11 Biological Role**

Nickel is a part of urease. [NiFe]-hydrogenases selectively oxidise H<sub>2</sub>. 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 (Ni<sup>0</sup>, Ni<sup>+</sup>) and or oxidized (Ni<sup>3+</sup>) 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/m<sup>3</sup> in

urban areas, although much higher levels 110 – 180 ng/m<sup>3</sup> 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/m<sup>3</sup> for elemental nickel, 0. 1 mg/m<sup>3</sup> for soluble inorganic nickel compounds and nickel subsulfide, 0. 2 mg/m<sup>3</sup> 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/m<sup>3</sup>) 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. NiCl<sub>2</sub> 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)<sub>4</sub> inhibits DNA dependent RNA synthesis activity by binding to chromatin or DNA and thereby preventing action of RNA polymerase, causing suppression 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 and 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,  $\text{NiCl}_2$ , nickel acetate  $\text{Ni}(\text{OCOCH}_3)_2$ , nickel nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and nickel sulphate,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  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,  $C_{32}H_{16}N_8Ni$  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 ( $C_8H_{14}N_4NiO_4$ ) 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-butylthiocarbamate nickel(II) complex,  $\text{Ni}[\text{CS}_2\text{N}(\text{C}_4\text{H}_9)_2]_2$  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.  $\text{Ni}(\text{OH})_2$  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 ( $\text{NiH}_2$ ) 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,  $\text{C}(\text{NH}_2)_2$  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, C<sub>3</sub>H<sub>8</sub>N<sub>2</sub>S 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  $\pi$  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.