**Chemistry of Chromium**

**Detecting chromium triple ion (Cr3+)**

Chromium triple solution can be prepared by dissolving CrCl3.6H2O in water to form green solution resulted from the complex ion [Cr(H2O)6]3+

**CrCl3.6H2O + H2O → [Cr(H2O)6]3+**

**Dark green solid Green clear solution**

This aqueous ion has an acidic characteristic in water:

**[Cr(H2O)6]3+ + H2O ↔ [Cr(H2O)5OH]2+ + H2O+ pKa= 4**

This ion can be abbreviated into (Cr3+) to carry out the following detections:

1. Put (10) drops of [Cr(H2O)6]3+ solution in a test tube, add (2) drops of NaOH, and observe the change, then add more of the detector and observe the change. then add (2) drops of H2O2 , observe the change, and heat the solution for 5 mints. and observe the change and write down your notices after each addition.
2. Put (10) drops of [Cr(H2O)6]3+ in a second test tube, add (2) drops of NH4OH, then add more of the a ammoni conc. and observe the change. Write down your notices in both cases.
3. Put (10) drops of [Cr(H2O)6]3+ in a third test tube, add (2) drops of Na2CO3 or K2CO3, observe the change and write down your notices.

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**Question:**

What is the distinguishable detection of Cr(III) Ion?

**Detecting anions :**

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A balance happens for the both anions Chromate (yellow) and Dichromate (orange) when a quantity of K2CrO4 and K2Cr2O7 is dissolved in water, according to the following equation:

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| **CrO42–(aq) + 2H+ ↔ Cr2O72– (aq) + H2O (L)** |  |

Chromate and dichromate solutions are prepared by dissolving Na2CrO4, Na2Cr2O7, K2CrO4, or K2Cr2O7 in water to compose a yellow or orange solution, respectively. It can be abbreviated into ( and ) to perform the following detections:

1. Put (10) drops of in a test tube and add (2) drops of NaOH, observe the change and write down your notices.
2. Put (10) drops of in a second test tube, add (2) drops of HCl, observe the change and write down your notices.
3. Put (10) drops of in a third test tube, add (2) drops of Pb(NO3)2 or Ba(NO3)2, observe the change and write down your notices.
4. Put (10) drops of in a test tube, add (2) drops of NaOH, observe the change and write down your notices.
5. Put (10) drops of in a second test tube, add (2) drops of HCl, observe the change and write down your notices.
6. Put (10) drops of in a third test tube, add (2) drops of Pb(NO3)2 or Ba(NO3)2, observe the change and write down your notices.

**Questions:**

1. What happen when HCl is added?
2. What happen when NaOH is added?
3. What happen when Pb(NO3)2 or Ba(NO3)2 is added?

**Preparation of Chromic Oxide (Cr2O3) :**

1. Gradually put (1) gr of the orange ammonium dichromate (NH4)2Cr2O7 in a crucible on flame, very soon you will see flash at each addition.

Cr2O3



1. Pull the flame away from the bowl when the flashing happens.
2. Return the flame again after flash end until the dichromate quantity is decomposed.

**Reaction Equation:**

**(NH4)2Cr2O7 ⎯ φ→ N2 ↑ + Cr2O3 + 4H2O**

**Questions:**

1. What the flash means?
2. Calculate the product percentage.
3. Why dichromate is gradually added?
4. What is the principle of this reaction?

**Preparation of Potassium Chromate:**

1. Melt a mixture of (3g) of KNO3 and (2g) of K2CO3 in porcelain crucible.
2. Add (0.5g) of Cr2O3 (prepared in step 1) gradually to the molten mixture.
3. Leave the mixture to melt on a Binzin lamp until it change from green to yellow.
4. Leave the bowl to cool down, then add (15 ml) of distilled water.
5. Heat and filter (neglect the precipitate).
6. Reduce the filtered solution by evaporating into 2/3 of the original volume.
7. Cool down and filter again to get K2CrO4.

**Reaction Equation:**

**2K2CO3 + KNO3 + Cr2O3 → 2K2CrO4 + 2CO ↑ + KNO2**

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| [Image result for crucibles chemistry](https://www.google.com/imgres?imgurl=http://www.rsc.org/learn-chemistry/wiki/images/2/23/TheChangesinMasswhenMagnesiumBurnsApparatus.PNG&imgrefurl=http://www.rsc.org/learn-chemistry/wiki/index.php?title=TeacherExpt:The_change_in_mass_when_magnesium_burns&oldid=5226&h=383&w=623&tbnid=DPjSr9CYF2cYqM:&docid=oA0I3ulxn3nf2M&ei=PC30VcOSMOSCygOH9ZGYBA&tbm=isch&ved=0CEwQMyglMCVqFQoTCMOgk7rR8ccCFWSBcgodh3oEQw) | F:\Pictures\200px-Potassium-chromate-sample.jpg |

**Questions:**

1. What is the purpose behind using a mixture of K2CO3 and KNO3?
2. Calculate the ratio of K2CrO4.

**Preparation of Potassium trioxalatochromate (III) trihydrate K3[Cr(C2O4)3].3H2O :**

1. Dissolve (2.5g) of H2C2O4 in (10ml) of hot distilled water.
2. Gradually add (0.5g) of K2Cr2O7.
3. Heat the mixture until boiling to complete reaction.
4. Dissolve (1.25g) of K2C2O4 in the hot mixture, then cool it down to room temperature.
5. Add (2ml) of ethanol and cool down using ice, you will notice separation of greenish blue crystals.
6. Filter the solution and collect the crystals using Büchner funnel.
7. Dry the resulted crystals at 60oC.
8. Measure the resulted material weight and calculate its ratio.

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The color-change from red cubic crystals to dark blue under fluorescent light, and to reddish violet under incandescent light.

**Questions:**

1. Why the Oxalic acid coordinates with the central metal in alkaline medium? What happen if the medium was acidic?
2. Why ethanol is added?
3. Why K2C2O4 is added? What happens if KOH was added?
4. Write down the reaction equation.

Notes: The student must write the following for each complex attended information

1. **Electronic configuration for the metal and its ion:**

For example:

Electronic configurationof Cr atom is

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| 24Cr: [18Ar] 3d54s1 | | | | | | | | | | | | |
|  |  |  |  |  |  |  |  |  |  |  |  |
| 3d | | | | |  | 4s |  | 4p | | |  |

Whereas the electronic configuration **of** Cr (III) ion is

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Cr3+ [18Ar] 3d3 4s0 | | | | | | | | | | | | |
|  |  |  |  |  |  |  |  |  |  |  |  |
| 3d | | | | |  | 4s |  | 4p | | |  |

1. **Type of hybridization of the central atom in the complex [Cr (C2O4)3]3- is d2sp3**

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Cr3+ [Ar]18 3d3 4s0 | | | | | | | | | | | | |
|  |  |  | ×× | *××* |  | ×× |  | ×× | ×× | ×× |  |
|  | | | | |  |  |  |  | | |  |
| ox | | | | |  |  | ox | Ox | | |  |

Where ox= (C2O4=), which is bidentate oxalate ligand

1. **Orbital type (d):**

Whether the given complex ion is inner orbital octahedral or outer or orbital octahedral?

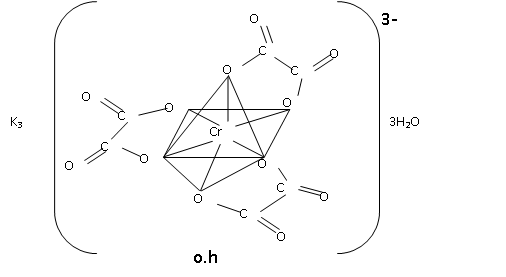
This complex is inner orbital octahedral.

1. **Magnetic properties:**

The metal in this complex is paramagnetic because of the existence of three single electrons.

1. **Geometry of complex:**

It is octahedral, where the oxalate ion (the ligand) connected with Cr(III) ion by both anionic donor atoms (o-,o-) according to the following structure:



**Chemistry of Iron**

Ferrous Fe (II) and Ferric Fe(III) form many complexes whose octahedral structure in which the coordination number is **six**; as in aqueous solutions of ferrous salts (FeSO4.6H2O)the complex ion [Fe(H2O)6]2+ is formed which is very light greenish blue. Whereas, the complex ion [Fe(H2O)6]+3 is formed in aqueous solutions of ferric salts (FeCl3.6H2O).

Fe(II) and Fe(III) form very little number of tetrahedral complexes, some are anionic such as [FeX4]2– and [FeX4]1–, others are neutral like [FeX2L2] and [FeX3L], and others are cationic such as [FeL4]+2 and [FeL4]+3.

Neutral ligand=L and X= Cl–, F–, Br–, and I–.

1. **Detection of iron** (II) **(Fe2|+)**
2. **Preparing a solution of (Fe2+):**

Iron solution can be prepared by dissolving ammoniac salt of Iron(II) sulfate (NH4)2SO4.FeSO4.6H2O or simple iron sulfate (FeSO4.6H2O) in acidic water with H2SO4 to form bluish light green solution due to the formation of [Fe(H2O)6]2+, which can be abbreviated into (Fe2+)to carry out detection.

(NH4)2SO4.FeSO4.6H2O + H2O → [Fe(H2O)6] 2+

Greenish gray solid clear bluish light green

FeSO4.6H2O + H2O → [Fe(H2O)6] 2+

Light blue solid clear bluish light green

1. **pH of Aqueous ferrous solution (Fe2+):**

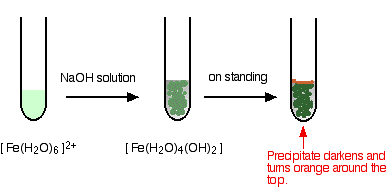
Put (10) drops of [Fe(H2O)2]2+ in a test tube and measure pH by using Litmus paper (the reaction starts before adding H2SO4, why?). you will notice that acidic solution is weak due to weak ionization.

1. **Ferrous Oxidation (Fe2+) Detectors:**
2. Put (10) drops of [Fe(H2O)6]2+ solution in a test tube, add hydrogen peroxide solution (H2O2) drop wise, observe the change, and write down your notices.
3. Put (10) drops of [Fe(H2O)6]2+ solution in a second test tube, add Potassium Permanganate solution (KMnO4) drop wise, observe the change, and write down your notices.
4. **Ferrous Ion (Fe2+) Detectors:**
5. Put (10) drops of [Fe(H2O)6]2+ solution in a test tube, add (2) drops of potassium ferric cyanide solution (K3[FeIII(CN)6]), you will notice a dark blue precipitate , and write down your notices.
6. Put (10) drops of [Fe(H2O)6]2+ solution in a second test tube, add (2) drops of Potassium ferro cyanide solution (K4[FeII(CN)6]), you will notice a white precipitate, and write down your notices (the precipitate will change to blue when exposed to air due to oxidation).
7. Put (10) drops of [Fe(H2O)6]2+ solution in a third test tube, add (5) drops of thio acetamide solution (CH3CSNH2), observe the change, add (3) drops of concentrated ammonia NH3(aq), you will notice a black precipitate, and write down your notices.
8. Put (10) drops of [Fe(H2O)6]2+ solution in a fourth test tube, add (2) drops of sodium hydroxide solution (NaOH), you will notice a blackish green precipitate, write down your notices.
9. Put (10) drops of [Fe(H2O)6]2+ solution in a fifth test tube, add (2) drops of concentrated ammonia NH3(aq), you will notice a blackish green precipitate, write down your notices.
10. Put (10) drops of [Fe(H2O)6]2+ solution in a sixth test tube, add (2) drops of sodium carbonates (Na2CO3), you will notice a green precipitate, write down your notices.
11. Put (10) drops of [Fe(H2O)6]2+ solution in a seventh test tube, add (2) drops of ammonium or Potassium thiocyanate ( (NH4SCN), observe the change, and write down your notices.
12. **Detection of iron (III) (Fe3+)**
13. **Preparing Solution of (Fe3+):**

This solution can be prepared by dissolving ferric chloride salt (FeCl3.6H2O) in water to form a yellow-orange solution due to formation of the complex ion [Fe(H2O)6]3+, which can be abbreviated as (Fe3+) to carry out detections.

1. **pH of Aqueous ferric solution (Fe3+):**

Put (10) drops of [Fe(H2O)6]3+ solution in a test tube, measure solution pH by using Litmus paper, you will observe that the solution is very acidic due to the previously mentioned ionization.

1. **Ferric Oxidation (Fe3+) Detectors:**
2. Put (10) drops of [Fe(H2O)6]3+ solution in a test tube, add hydrogen peroxide solution (H2O2) drop wise, observe the change, and write down your notices.
3. Put (10) drops of [Fe(H2O)6]3+ solution in a second test tube, add Potassium Permanganate solution (KMnO4) drop wise, observe the change, and write down your notices.
4. **Ferric Ion (Fe3+) Detectors:**
5. Put (10) drops of [Fe(H2O)6]3+ solution in a test tube, add (2) drops of potassium feeric cyanide solution (K3[FeIII(CN)6]), you will notice a brown precipitate , write down your notices.
6. Put (10) drops of [Fe(H2O)6]3+ solution in a second test tube, add (2) drops of Potassium ferrocyanide solution (K4[FeII(CN)6]), you will notice a blue precipitate, write down your notices.
7. Put (10) drops of [Fe(H2O)6]3+ solution in a third test tube, add (5) drops of thioacetamide solution (CH3CSNH2), observe the change, add (3) drops of diluted hydrochloric acid HCl, you will notice a white yellowish sediment, write down your notices.
8. Put (10) drops of [Fe(H2O)6]3+ solution in a fourth test tube, add (2) drops of sodium hydroxide solution (NaOH), you will notice a dark brown sediment, write down your notices.
9. Put (10) drops of [Fe(H2O)6]3+ solution in a fifth test tube, add (2) drops of the concentrated ammonia NH3(aq), you will notice a dark brown sediment, write down your notices.
10. Put (10) drops of [Fe(H2O)6]3+ solution in a sixth test tube, add (2) drops of sodium carbonates (Na2CO3), observe the change, and write down your notices.
11. Put (10) drops of [Fe(H2O)6]3+ solution in a seventh test tube, add (2) drops of ammonium (or Potassium) thiocyanate ( (NH4SCN), you will observe a dark red solution, write down your notices.

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**N.B:** write down all reactions products.

**Questions:**

1. Which one is more acidic ion of ferrous aqueous complex or ferric aqueous complex? Why?
2. Which detection is considered a distinguish one for ferrous ions? Why?
3. Which detection is considered a distinguish one for ferric ions? Why?
4. Distinguish, using a laboratory reaction, between Fe(II) and Fe(III) ions?
5. What is Prussian blue and Trunbull blue? Write the chemical formula, and the preparation equation of each one. Mention their industrial uses.

**Preparing potassium trioxalatoferrate (III) trihydrate K3[Fe(C2O4)3].3H2O**

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| http://imgfrm.index.hu/imgfrm/1/8/0/9/THM_0008811809.png | **E:\dddddd\حديد\Potassium ferrioxalate - Wikipedia, the free encyclopedia_files\300px-2-isomers-of-ferrioxalate.svg.png** |

1. Dissolve (2.5) of ammoniac salt of Iron(II) sulfate (NH4)2SO4.FeSO4.6H2O in a backer consists of (10) drops of hot distilled water after acidizing the water with (H2SO4).
2. Dissolve (1.25g) of dehydrate oxalic acid H2C2O4.2H2O in a packer consists of (10ml) of hot distilled water.
3. Add the contents of backer in step 2 to the contents of the packer in step 1, heat the mixture to boil leave the yellow sediment represented by ferrous oxalate to stagnate for (5-10)mints.
4. Carefully pour the clear liquid and add to the sediment (8ml) of hot distilled water, stir the mixture, and then filter it.
5. Move the sediment that in the filtering paper to a packer, add (5ml) of hot distilled water that contains (1.75g) of potassium oxalate K2C2O4.H2O.
6. Using a dropper, slowly add (4ml) of hydrogen peroxide H2O2 to the mixture with continuous stirring during the addition (keeping solution temperature 40oC).
7. Boil the mixture, dissolve the brown sediment ferric hydroxide Fe(OH)3 by adding (10ml) of oxalic acid (H2C2O4), which is prepared by dissolving (0.5g) of the acid in (15) ml of distilled water, then add the remaining (5ml) of the acid drop wise until ferrous hydroxide completely dissolves, during the add mixture temperature should be close to boiling.
8. Filter the hot solution, add (10ml) of ethanol (C2H5OH) to the filtrate neglecting the precipitate (dissolve the formed crystals ,then heat the solution, heat using water bath).
9. Leave the solution in a dark place for 24 hrs.
10. Filter the crystals using Büchner funnel, wash with (1:1) (alcohol:water), then wash with acetone, weight the resulted material, and calculate the ratio.

**Reaction Equation:**

**(NH4)2SO4.FeSO4.6H2O + H2C2O4.2H2O + K2C2O4.H2O + H2O2 → K3[Fe(C2O4)3].3H2O + H2O + ?**

**Questions:**

1. What is the benefit of adding:
2. K2C2O4.H2O b. H2O2 c. EtOH
3. What is the purpose of adding aqueous oxalic acid H2C2O4 twice?
4. What is the oxidizing and reducing agent in this experiment? Why?
5. What the water contains in step (4)?
6. Write down complex preparation equation.
7. Why we wash using alcohol, water and then by acetone?
8. What will happen if we change K2C2O4.H2O by KOH? Does the reaction will continue? If yes, write the reaction equation.
9. In some students’ experiments, a yellow layer appeared on the green precipitate, what this layer? Write a full balanced equation.
10. Is the prepared complex isomer? If yes, what kind?

**Note:** The student has to write the following information about each prepared complex.

1. Electron configuration for the central atom and its ions.
2. Hybridization of the central atom in the complex
3. The type of orbital (d).
4. The magnetic properties.
5. Complex geometry.
6. Complex color and crystal shape.

The complex [Fe(C2O4)3]3- is a stereoisomer so it has an optical activity, as it can rotate the polarized light level that goes through them one rotate it to the right (**Δ, d**) and the second rotate it to the left (**Λ,L**) and both have the same amount. Also, when we shed light on the complex it will undergo photo-reduction, by which it would absorb a photon of light and subsequently decomposes to form Fe(C2O4)22- and CO2, i.e., iron center is to be reduced (gains an electron) from the +3 to the +2 oxidation state while an oxalate ion is oxidized to carbon dioxide:

**[Fe(C2O4)3]3- + *hv* → [Fe(C2O4)2]2- + 2 CO2**

**Preparation of Sodium ethylenediaminetetraacetatoferrate (III) trihydrate Na [Fe (EDTA)].3H2O:**

1. **Dissolve (0.4 g) of sodium hydroxide in a beaker consists of (10 mL) of water then add (3.8g) of Na2H2EDTA.2H2O solution to the beaker. Heat the mixture gently until the solid dissolves.**
2. . **Dissolve (2.5 g) of iron(III) chloride hexa hydrate in (5 mL) of water in other beaker.**
3. **Pour the iron(III) chloride solution into the beaker( step 1), stirr the mixture**.
4. **Warm the mixture until the boiling , evaporate gently some of the water until a yellow powder precipitates appears , this may take about five minutes**.
5. **Let the mixture cool, collect and filter the precipitate , wash it well with ice-cold water and ethanol , Dry the resulted crystals, weight and calculate the ratio**.

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| **EDTA** | **EDTA4-** | **[Fe(EDTA)]-** |  | |

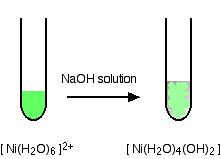
**Questions:**

1. What is the benefit of using NaOH?
2. Which of these ligands is a chelate (OH-, CN-, and H2NCH2CH2NH)?
3. Does this experiment depend on oxidation and reduction principle?
4. Write down this complex preparation equations.

**Chemistry of Nickel**

Nickel (II) forms many complexes whose different coordination numbers (4, 5, and 6) like:

* C.N=4 [Ni(X)4]2– tetrahedral / Ni(DMG)2 square planer.
* C.N= 5 [Ni(CN)5]3− square pyramid.
* C.N=6 , [Ni(H2O)6]2+ octahedral, which is green.

**Detection of Nickel ion (+2):**

1. **Preparing (Ni2+) Solution:**

The solution is prepared by dissolving(1g)of nickel sulfate NiSO4.7H2O or nickel chloride salt NiCl2.6H2O in water to form a green solution due to formation of the complex ion [Ni(H2O)6]2+, which can be abbreviated (Ni2+) to carry out the following detections:

**NiSO4.7H2O + H2O → [Ni(H2O)6]2+**

Greenish gray solid green clear solution

**NiCl2.6H2O + H2O → [Ni(H2O)6]2+**

Gray green sold green clear solution

1. Put (10) drops of [Ni(H2O)6]2+ solution in a test tube, add (2) drops of sodium hydroxide NaOH then heat the solution and write down your notices.
2. Put (10) drops of [Ni(H2O)6]2+ solution in a second test tube, add (2) drops of ammonium hydroxide NH4OH then add some more of the detector, observe the change, and write down your notices.
3. Put (10) drops of [Ni(H2O)6]2+ solution in a third test tube, add (5) drops of thio acetamide CH3CSNH2, observe the change, and write down your notices then add (2) drops of the concentrated Ammonia solution NH3(aq), observe the change, and write down your notices.
4. Put (10) drops of [Ni(H2O)6]2+ solution in a forth test tube, add (2) drops of ammonium (or Potassium) thiocyanate (NH4SCN), observe the change, and write down your notices.
5. Put (10) drops of [Ni(H2O)6]2+ solution in a fifth test tube, add (2) drops of alcoholic dimethyl glayoxim (C4H7O2N2 (DMG)) (5%), then add (2) drops of the concentrated ammonia solution NH3(aq), observe the change, and write down your notices.

**Preparing Nickel Complexes:**

1. **Preparation of hexaamminenickel(II) chloride complex Ni(NH3)6]Cl2 (II) :**
2. Dissolve (3g) of the green nickel (II) chloride hydrous NiCl2.6H2O in (5ml) of hot water in a backer (150 ml), then cool down the solution.
3. Add (5.8ml) of the concentrated Ammonia (NH3conc.) with stir, cool down using icy bath, tap the backer walls continuously.
4. Add more of the concentrated Ammonia (NH3conc.) until the purple crystals of the complex are completely separated down and the solution color changes to light blue or colorless, with continuous cooling.
5. Add (15ml) of cold ethanol or acetone to crystalize the complex, leave the solution for (10) mints. in icy bath.
6. Filter the crystals using Büchner funnel, wash them using diluted cold ammonia, and then wash gradually using (5ml) cold ethanol.
7. Dry, calculate the ratio for the resulted complex.

**Reaction Equation:**

**NiCl2.6H2O (aq) + NH3 (conc.,aq) → [Ni(NH3)6]Cl2 + 6H2O**

1. **Preparation of Bis(dimethylglyoximato) nickel(II) [Ni(C4H7O2N2)2] :**
2. Weight (0.3g) of the above complex [Ni(NH3)6]Cl2 in (500ml) backer, add (5ml) of HCl (6M), then dilute the solution with distilled water to be (200ml).
3. Heat the mixture to 75oC.
4. Add (35ml) of alcoholic dimethyl Glycoxim (DMG) (5%) solution (C4H7O2N2).
5. Add the concentrated Ammonia NH3(aq) drop wise with continuous stir until the red precipitate is formed, then add (20) additional drops.
6. Heat the mixture using water bath for (25) minutes, be sure that precipitate is complete by adding some more drops of (DMG) solution.
7. Filter the solution, and dry it at (100-120)oC.
8. Weight the product and calculate its ratio.

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**Chemistry of Cobalt**

**Cobalt ion Reactions**:

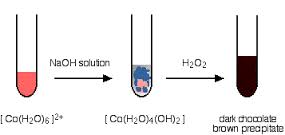
**Detecting Cobalt(II) Ion (Co2+) :**

This solution is prepared by dissolving (1g) of cobalt (II) nitrate Co(NO3)2.6H2O in water to form a reddish pink solution due to forming complex ion [Co(H2O)6]2+:

**Co(NO3)2.6H2O + H2O → [Co(H2O)6]2+**

**Dark pink solid reddish pink clear solution**

This ion can be abbreviated as (Co2+) to carry out the following detections:

1. Put (10) drops of [Co(H2O)6]2+ solution in a test tube, add (2) drops of sodium hydroxide (NaOH), observe the change, divide the product into two quantities, heat one of them for (5) mints., and observe the change. Add (2) drops of hydrogen peroxide (H2O2) to the second quantity, observe the change, and write down your notices after each addition.
2. Put (10) drops of [Co(H2O)6]2+ solution in a second test tube, add (2) drops of ammonia hydroxide (NH4OH), then add some more of the same detector, observe the change, and write down your notices in both cases.
3. Put (10) drops of [Co(H2O)6]2+ solution in a third test tube, add (2) drops of sodium or potassium carbonate (Na2CO3), observe the change, and write down your notices.
4. Put (10) drops of [Co(H2O)6]2+ solution in a fourth test tube, add (2) drops of ammonium (or potassium) thiocyanate (NH4SCN), observe the change, then add drops of acetone, observe the change, and write down your notices.
5. Put (10) drops of [Co(H2O)6]2+ solution in a fifth test tube, add (5) drops of thioacetamide solution (CH3CSNH2), observe the change, add (3) drops ammonia solution (NH4OH), observe the change, then heat the mixture, observe the change, and write down your notices.
6. Put (10) drops of [Co(H2O)6]2+ solution in a sixth test tube, add (2) drops of acetic acid (CH3COOH), observe the change, add (2) drops of sodium nitrite (NaNO2), observe the change and write down your notices after each addition.
7. Put (10) drops of [Co(H2O)6]2+ solution in a seventh test tube, add (2) drops of alcoholic dimethyl glycoxim (C4H7O2N2 (DMG)) (5%), write down your notices, then add (2) drops of ammonia solution, what do you notice?

**Questions:**

1. What is the distinguished detection for Cobalt ions?
2. In which of the above mentioned detections Co(II) was oxidized to Co(III)?
3. Why Co(II) salts are stable whereas Co(III) complexes are more stable?

**Preparing Some Cobalt Complexes:**

**Preparation of Sodium Tricarbonitocobaltate(III) Trihydrate Na3[Co(CO3)3].3H2O:**

* **Theory:**

Carbonate ion () is considered one of the bidentate ligands due to two coordination connection with the central metal, which is a plane regular molecule whose structure:

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In this ion, carbon associates with oxygen atom by π double bond and with two oxygen atoms by σ single bond, as each atom has one negative charge by which it coordinates with the metal ion. The complex is olive green powder, does not dissolve in water, stable when it is dry and decomposes at 93oC without melting.

* **Procedure:**

1. Dissolve (1.5g) of aqueous cobalt nitrate (Co(NO3)2·6H2O) in (2.5ml) of distilled water, and then add (0.5ml) of Hydrogen peroxide (30%).
2. In another packer, dissolve (1g) of sodium carbonate (NaCO3) in (7.5ml) of distilled water (if did not completely dissolved, heat the solution until completely dissolves).
3. Cool down the solution prepared in step (2) using icy bath until it reach 0oC, then add the solution prepared in step (1) drop wise throughout (10) minutes. with continuous stirring, continue stir for (30) mints. keeping the mixture in the icy bath (0oC).
4. Filter the formed dark green precipitation, wash it with ethanol, and then dry the precipitation (be careful not to leave any humidity as it would be decomposed into black solid material.
5. Calculate the ratio of the resulted complex.

**Reaction Equation:**

**Co(NO3)2.6H2O + H2O2 + 10NaHCO3 ⎯→ 2Na3[Co(CO3)3].3H2O + 4NaNO3 + 4CO2 + 12H2O**

**Questions:**

1. Why hydrogen peroxide and sodium bicarbonate are added?
2. Why we wash using ethanol and then using ether?

# Preparation of Mercury(II) Tetraisothiocyanatocobaltate(II)

**Hg]Co(NCS)4]:**

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| co-2 |  |

**Procedure:**

1. In a backer put (2g) of cobalt chloride hexa hydrate (CoCl2.6H2O) with (2.2g) of ammonium thiocynate.
2. Add (4ml) of boiling distilled water to the backer, dissolve the solid materials with keeping high temperature below boiling (backer -1).
3. In another backer dissolve (1.9g) of mercury(II) chloride in (24ml) of distilled water, boil the solution to help dissolving, filter if the solution was not clear (backer -2).
4. Add backer -1 contents to backer -2, mix the solution, and boil for (3) minutes.; a dark blue solution will be formed.
5. Leave the solution to cool, filter and wash the precipitate with water and ethanol, dry at 110oC.
6. Calculate the ratio of the resulted complex.

**Reaction Equation:**

**CoCl2.6H2O + 4NH4SCN + HgCl2 ⎯→ Hg]Co(NCS)4] + 4NH4Cl+ 6H2O**

**Questions:**

1. Compare Na3[Co(CO3)3].3H2O with Hg[Co(NCS)4] for hybrid, center ion oxidative case, geometry, ligands type, magnetic characteristic, coordination number, counter ion type, and crystal color.
2. Does this reaction depend on oxidation and reduction principle?
3. What is the benefit of boiling and using mercuric chloride?
4. In the following two figures there are tetrahedral and octahedral structures; complete them to calculate stabilizing energy of crystal space for Co complexes that prepared according to these structures, and show which one is more stable.

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**Preparation of Hexaammincobalte(III) chloride**

**[Co(NH3)6]Cl3** :

**Procedure:**

1. Dissolve (0.5g) of ammonia chloride in (3ml) of distilled water, and then heat the solution.
2. Gradually, dissolve (2.5g) of cobalt(II) chloride, in step (1) solution.
3. In another dry and clean backer put (0.5g) of charcoal, and add the solution prepared in steps (1 and 2) with stir.
4. Cool down the mixture in cold water, add (5ml) of concentrated ammonia, and then cool down the mixture in icy bath.
5. Gradually, add during cooling (4.5ml) of hydrogen peroxide (H2O2) (30%) with continuous stir.
6. When you finish, heat the mixture to 60oC (do not exceed this temperature), with shaking from time to time for around (20) minutes.
7. Cool down the mixture using icy bath, you will notice separating precipitate crystals.
8. Put in another backer (17.5ml) of distilled water, add (1ml) of the concentrated HCl, then boil the mixture, during boiling add the precipitate formed in step -6.
9. Continue heating and stir until the sediment dissolves and nothing of charcoal stays, and then filter the hot solution.
10. Add (1ml) more of the concentrated HCl.
11. Cool down the filtrate, collect the crystals, and dry them neglecting the precipitate (charcoal).
12. Calculate the ratio of the resulted complex.

**Reaction Equation:**

**2CoCl2.6H2O + 2NH4Cl + 10NH3 + H2O2 → 2[Co(NH3)6]Cl3 + 4H2O**

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**Questions:**

1. What is the benefit of using animal coal?
2. Why hydrogen peroxide is added?
3. What is the benefit of adding the concentrated ammonia?
4. Why the reaction is carried out in glacial bath?
5. Why when peroxide is added temperature should be 60oC?
6. Why the concentrated HCl is added?

**N.B:**

The following information should be written for each prepared complex:

1. Electron configuration of the central atom and its ion.
2. The central atom hybrid in the complex.
3. Orbital d type.
4. Magnetic properties.
5. Complex Geometry.
6. Complex color and crystal shape.

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| **Isomersim among Coordination Compounds**  **(Isomers)** |
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**Geometrical Isomers**

1. **Preparation of Trans-dichlorobis(ethylenediammine)cobalt(III) chloride [Co(en)2Cl2]Cl:**

Isomer trans can be prepared by oxidizing Co(II) to Co(III) in the existence of H2O2, which starts with Co(II) not Co(III) because Co(III) salts are not stable and have the ability to react with water and reduce to Co(II) according to the following equation:

**4Co+3(aq) + 2H2O → 4Co+2(aq) + 4H+(aq) +O2(g)**

1. Dissolve (4g) of aqueous cobalt(III) chloride in (10ml) of distilled water.
2. Add (15ml) of ethylene diamine (10%) with stir, then cool down the solution using ice for (20) minutes.
3. Add (15ml) of hydrogen peroxide (6%) (H2O2) drop wise to the solution with stir for (15) minutes. and keep solution temperature below 10oC during addition.
4. Leave the solution for (10) minutes. at room temperature, and then heat it to 40oC for (5) minutes.
5. Slowly, add (8ml) of concentrated HCl drop wise for (25) minutes.
6. Vaporize the solution at 100oC until its volume become (20ml) when a green precipitation will be formed in the solution.
7. Leave the solution for 24 hrs to let the shiny green sediment to form, then filter it and ensure filtration tools dryness because the sediment dissolves in water.

Co

en

Cl

Cl

en

.Cl

1. Wash the formed precipitation with (10ml) of ethyl alcohol, and then with ether.
2. Dry the sediment by oven at 75oC for 30 minutes. until the crystals become dark green powder.
3. Weight the precipitation, which represents trans complex, and calculate its ratio.

**Reaction Equation:**

**2CoCl2 + 4en + 2HCl + H2O2 → 2trans[Co(en)2Cl2]Cl + 2H2O**

**Questions:**

1. Why we start with Cobalt(II) chloride (Co2+) as a source to get the central metal and we did not start with cobalt(III) (Co+3) in spite of the fact that we want to prepare cobalt(III) comlexes?
2. What is the purpose of adding:

Ethylene diamine, hydrogen peroxide, concentrated HCl.

1. Why the precipitate is washed with ethanol and then with ether?
2. **Preparation of Cis-dichlorobis(ethylenediammine)cobalt(III) chloride [Co(en)2Cl2]Cl:**
3. Weight (1g) of the dry trans isomer (prepared in paragraph 1) in a small backer and dissolve with least quantity of distilled water, neutralize acidic solution by gradually adding diluted ammonia.
4. Vaporize the solution in water bath dryness until and it becomes purple (change to Cis).
5. If part of the trans isomer did not change to cis repeat the procedure (dissolve the precipitate again in water and neutralize the solution using ammonia and vaporize it to dryness), until it become purple.
6. Weight the formed precipitation (cis complex) and calculate the ratio and draw the resulted complex structure.

**Questions:**

1. What is the purpose of using ammonia?
2. Which of the following is trans isomer:

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1. **Preparation of Potassium cis-dioxalatodiaquachromate(III) dihydrate Cis-K[Cr(C2O4)2(H2O)2].2H2O):**
2. Mix (12g) of aqueous oxalic acid with (4g) of potassium dichromate, grind the mixture using ceramic mortar, and continue gridding until you get homogeneous mixture.
3. Moisten a ceramic bowl with distilled water and put the mixture powder and cover it with watch glass.
4. Put the ceramic bowl on a quiet hot slab and wait for a small period, as a rapid and continuous reaction will start leading to form a dark and heavy liquid.
5. Add to the dark liquid (20ml) of ethanol and crush contains using a metal spoon until it solidify.
6. Filter the solution to get granular crystals represents cis isomer.
7. Weight the precipitation (cis complex) and calculate the ratio.

**Reaction equation:**

**K2Cr2O7 + 7H2C2O4.2H2O → 2Cis-K[Cr(C2O4)2(H2O)2] .2H2O +13H2O +6CO2↑**

**Questions:**

1. What is the purpose of using oxalic acid and potassium dichromate?
2. What is the shape and color of the produced crystals? and what is the reaction type and preparation method?
3. **Preparation of Potassium trans-dioxalato diaqua chromate(III) dihydrate , trans-K[Cr(C2O4)2(H2O)2].2H2O:**
4. Mix (12g) of aqueous oxalic acid with least quantity of hot distilled water in a backer, and dissolve (4g) of potassium dichromate in least quantity of hot distilled water in another backer.
5. Add dichromate solution to oxalic solution and cover the backer with watch glass after each addition and stir to continue the reaction, and then leave the solution to cool down for (24) hrs.
6. Filter the solution, wash the crystals with (5ml) of distilled water, and then with ethanol to get trans isomer.
7. Dry the formed precipitation , and calculate the ratio of the complex.

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**Questions:**

1. Compare between trans-K[Cr(C2O4)2(H2O)2].2H2O and Cis-K[Cr(C2O4)2 (H2O)2].2H2O.
2. Write down the oxidation and reduction equations for both complexes.

**Linkage Isomers**

Linkage isomer appears when the ligand has two different atoms having the ability to coordinate (i.e., the ligand has more than one donor atom); the coordination will be between the metal and the ligand via one of the two atoms and other isomer via the other atom for the same ligand, as follows:

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|  | bonding via N nitro- bonding via O nitrito- |
|  | bonding via S → thiocyanato- bonding via N → isothiocyanato- |
|  | bonding via C → cyano- bonding via N → isocyano- |

**Linkage nature depends on several factors:**

* Reaction temperature.
* Method of adding the reacted materials.
* pH of the reaction (adding the ligand in an acidic or alkaline or neutral).
* Metal nature and type, for instance the first transitional elements prefer linkage through nitrogen atom, while the second transitional elements prefer linkage via sulfur of oxygen.

**Preparation of Pentaamminechlorocobalt(III) chloride [Co(NH3)5Cl]Cl2:**

**NB.: this experiment should be done inside the hood.**

**Procedure:**

1. Dissolve (5g) of the cobalt (II) chloride hydrous CoCl2.6H2O in least distilled water in a backer, it may require heating.
2. In another packer, dissolve (10g) of ammonium chloride in (60ml) of concentrated ammonia.
3. Add the second backer contents to the first packer, you will notice a pink-yellow sediment of hexaaminechloridecobalt (III) [Co(NH3)6]Cl3, with heat emission.
4. Add (2.5ml) of hydrogen peroxide (30%) (H2O2), then add (2.5ml) of peroxide partially with stir (avoid the heat, as the reaction causes heat emission), after effervescence a red solution of pentaamineaquacobalt (III) chloride salt [Co(NH3)5(H2O)]Cl3 will be formed.
5. After oxidation, neutralize the solution by adding (30) drops of the concentrated HCl drop wise.
6. Heat the mixture on a hot plate for (20) minutes. (keep reaction temperature 85oC), and leave it to cool down.
7. Put the mixture inside icy bath, and separate the purple magenta sediment using Büchner funnel.
8. Wash the product with little of icy distilled water (not more than 15 ml), then wash with (15ml) of diluted HCl (6M).
9. Dry the precipitate using oven for (20) minutes., then weight it to calculate the ratio of the resulted complex, and then used as a base material to prepare the associative isomer.

**Questions:**

1. What is the reason behind using ammonium chloride and concentrated ammonia mixture?
2. What is the reason behind adding the following materials:

Peroxide, concentrated HCl, and ammonium hydroxide (20%)

1. Give the product of the following reactions:

* 2CoCl2⋅6H2O(s) + 2NH4Cl(s) + 10NH3(aq) + H2O2(aq) + 3H2O(l) charcoal
* 2CoCl2⋅6H2O(s) + 2NH4Cl(s) + 8NH3(aq) + H2O2(aq) + 3H2O(l) →

1. **Preparation of Nitropentaamminecobalt(III) chloride [Co(NH3)5NO2]Cl2 :**

**Procedure:**

1. Dissolve (1.25g) of the purple chloropentaaminecobalt(III) chloride complex that is previously prepared in (10ml) of distilled water in Erlenmeyer flask.
2. Add (1ml) of the concentrated Ammonia, then heat the contents with continuous stir for not less than (5) minutes. using water bath at 50oC.
3. Filter the resulted hot mixture, and neglect the sediment to get rid of insoluble part of chloropentaaminecobalt(III) chloride .
4. Cool down the filtrate at lab. Temperature, and acidize it using diluted HCl (2M) drop wise.
5. Weight (1.5g) of sodium nitrite NaNO2, and add it partially, you will notice after minutes of finishing the addition red precipitation formation, leave the mixture at lab. Temperature for not less than (5) minutes to complete precipitation.
6. Heat the mixture to dissolve the red precipitation, if did not completely dissolved; get rid of insoluble by filtration.
7. Slowly add to the filtrate the concentrated HCl drop wise for not less than 30 minutes.
8. Cool down the mixture using icy bath, you notice yellowish brown precipitation, collect it by filtration.
9. Dry the precipitation by oven, weight it, calculate its ratio, and draw its structure.

**Reaction equation:**

**[Co(NH3)5Cl]Cl2 + H2O + NH3 + HCldil. + NaNO2  →**

**[Co(NH3)5(NO2)]Cl2 + NaCl + NH4Cl+ H2O**

**Questions:**

1. What is the medium used for preparing the isomer?
2. What is the reason behind using water bath at 50oC in the second step?
3. **Preparation of Nitritopentaamminecobalt(III) chloride [Co(NH3)5ONO]Cl2:**
4. Dissolve (1.25g) of the purple chloro pentaaminecobalt(III) chloride complex that previously prepared in a warm mixture consists of (20) ml of distilled water and (4.5ml) of concentrated ammonia in an Erlenmeyer flask.
5. Filter the solution to get rid of insoluble chloropentaaminecobalt(III) chloride.
6. Neutralize the filtrate by adding diluted HCl (2M) drop wise, and neglect the precipitation.
7. Weight (1.2g) of sodium nitrite NaNO2, dissolve it in the solution with continuous stir.
8. Add to the product (1.2ml) of HCl (6M).
9. Leave the mixture aside to cool down to room temperature for not less than (15) minutes, so reddish orange precipitation will be formed.
10. Filter the solution and wash the precipitation with (5ml) of cold distilled water.
11. Dry the sediment by oven at 60oC for not less than 1 hr., weight it and calculate its ratio.

**Reaction equation:**

[Co(NH3)5Cl]Cl2 + (H2O+NH3)mixture+ HCldil.+ NaNO2→ [Co(NH3)5(ONO)]Cl2

**Questions:**

1. What is the reason behind using the following:
2. Warm mixture of concentrated ammonia and water.
3. Sodium nitrite.
4. Compare between [Co(NH3)5(NO2)]Cl2 and [Co(NH3)5(ONO)]Cl2.

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|  |  | **(a)** | **(b)** |

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| Element | Symbol | Existence in the Nature | Oxidation Cases | Physical Properties | Chemical Properties | Oxides |
| Chromium | Cr | Chromite (Cr2O3.FeO) it most important ore, which is complication of Fe(III) and Cr(III) dioxide  [http://www.oocities.org/fahad8002000/chromit1.jpg](http://www.google.com/url?sa=i&rct=j&q=&esrc=s&source=images&cd=&ved=0ahUKEwjZ1f-xkovMAhXoDZoKHYHXDaoQjRwIBw&url=http://www.oocities.org/fahad8002000/oreminrl.htm&psig=AFQjCNEc8vUplQZPXoYIxs_wDv0Ic-ioGA&ust=1460620692706878) | 52Cr24 =[Ar]18 3d5 4S1  Cr6+=[Ar]18 3d0 4S0  is a strong oxidation factor because it easily become Cr3+= [Ar]183d34S0  it is the most stable case Cr2+= [Ar]183d44S0  it is a strong reduction factor which easily oxidate into Cr+3, whereas Cr4+ Cr5+ have no solutions chemistry and suffer disproportionate into Cr3+, Cr6+ | White shining metal, cruel and breakable, but it loses its luster when heated. Also, it can be characterized by its chemical sluggishly evident in the normal temperature | Chrome directly unites with halogens, sulfur, nitrogen, carbon, silicon, boron and others at high temperatures.  Cr12% is used in stainless steel alloy industry, which enhances its cruelty, durability and resistance against corrosion and oxidation. Its compounds (K2 or Na2Cr2O7) is used as a cleaner for glassware after the adding the concentrated H2SO4, due to formation of a red precipitate CrO3 (+6) whose aqueous solution is considered a strong oxidizing material that have a strong potential for removing dirt:  Na2Cr2O7  + H2SO4  ↓  2Na+ + H3O+ + 3H2SO4 + CrO3 | CrO3 is red and its structure is    CrO2 is charred black and its structure is    Cr2O3 is dark green and its structure is    CrO is charred red and its structure is    Q/ which one of the above mentioned oxidants has acidic or amphoteric characteristics? Why? |
| Iron | Fe | Iron comes after aluminum in terms of abundance in nature as it constitutes 5% of the earth crust weight. It can b found in many oxidants forms, the most important are Magnetite (Fe3O4),    hematite (Fe2O3),    limonite (Fe2O3.H2O) or (FeO (OH)),    Siderite (FeCO3) and Pyrite (FeS2). Currently, it is believed that iron and nickel are the main components of earth core. | 56Fe26=[Ar]18 3d64S2 is the highest oxidation state.  Fe2+=[Ar]183d44SoFe3+=[Ar]183d54S0  are the most important ones.  Fe(II) is a good reduction factor whose oxidation stress  Fe+3 + e → Fe+2 (E° = + 0.77 V)  Whereas, molecular oxygen oxidizes ferrous to ferric in acid or alkaline solutions  2Fe+2 + ½ O2 + 2H+  ↓  2Fe+3 +H2O  (E° = + 0.46 V)  Fe6+=[Ar]18 3d2 4S0  The highest oxidation state of iron, which is unusual, is ferrate (FeO4)-2 that is magenta in solution and it is stable in alkaline  2NaOH + 2NaClO + 2Fe(OH)3 → 2Na2FeO4 + 2NaCl +2H2O  it slowly decomposes in acid  [FeO4]–2 + 2H2O → Fe2O3 + 2OH– + 2O2  Ferrate ion is considered one of the strong oxidation factors, which is able to oxidize ammonia to nitrogen. | Pure iron is gray, has a metallic luster, melts at 1528oC, and magnetic is the most important distinguishing characteristic of it. | Iron has an average chemical activity in the normal condition. It does not react in dry media, yet it become very active when heated, especially if it was powder. It easily dissolve in metallic acids producing hydrogen gas and (FeII) without air, and (FeIII) with air  Fe + 2 H3O+  ↓  Fe+2 +H2 + 2 H2O | Iron forms three oxides: FeO (black), Fe2O3 (reddish brown), and Fe3O4 (red). |
| Nickel | Ni | Carnierite [Ni(Mg)6SiO4(OH)8], and Pyrrhotite are the most found compounds of nickel    Most meteors consist of nickel as an iron and nickel alloy. It is believed that earth core consists of huge quantity of nickel. | 58Ni28=[Ar]18 3d8 4s2  Nio=[Ar]3d84s2, O.N=(0)  especially with π ligands like  Ni(CO)4  Ni1+= [Ar]3d84s1, O.N =1+  Its compounds are little and unstable, the most stable one is Ni(pph3)3X where I, Br, Cl=X  O.N =+3,+4  like NiO(OH)x, which is black powder.  Ni2+=[Ar]3d84s0, O.N =+2  The most stable state and has many aqueous salt compounds like:  Ni(ClO4)2.6H2O NiSO4.6H2O  Compound which has 4, 5, and 6 coordinating numbers like:  K2[Ni(CN)4]  [Ni(CN)5]−3  Ni(H2O)6+2 | It is silver, its magnetic is less than iron, it can be forged, reformed, and polished, and it can transmit electricity and temperature. | Can be used to protect metals, why?  Due to its average chemical activity and it does not react with air and water at usual temperature degrees.  It is considered an excellent motivator in hydrogenation reactions, why?  Because it absorbs high temperature of hydrogen, and it does not form compound with the absorbed hydrogen. | Nickel(II) oxide, NiO, green.  Nickel(III) oxide, Ni2O3, black |
| Cobalt | Co | Cobaltite CoAsS, Smaltite CoAs2 | 27 Co58 =[Ar]18 3d74s2  Its oxidation is between (-1)-(+4)  o.N=1-, [Ar]3d84s2  like [Co(CO)4]−.  o.N=+1,[Ar]3d74s1  forms compound most of them π bonds.  o.N=+4, C.N=6 [Ar]3d54s0 like in [CoF6]−2octahedral  but its most famous and important oxidation state is  O.N=+2,[Ar]3d74s0  O.N=+3,[Ar]3d64s0  - Why it is easy to convert Co(II) to Co(III) in compounds?  - Why Co(III) salts are difficult to be prepared?  - why Co(III) ion is unstable in aqueous solutions? | Grey to blue shining metal, melts at 1493oC, and boiling at 3100oC | In the normal temperature, it does not affect with air, water; yet if it was powder it reacts with them. It slowly dissolves in the diluted acids, while is does not dissolve in the oxidant and concentrated ones, due to the formation of protecting layer that stops the reaction. This metal tends to form ions and complex compounds more than other elmts. | CoO, Co2O3, Co3O4  Co3S4, CoS2, CoS  Also, there are other halogens compounds of cobalt, the most important is CoCl2. |