Exp. 9

AIM: Nickel - Complex synthesis and estimation.

Apparatus Required: Burette, pipette, conical flasks, beakers, droppers, measuring cylinders, vol. flasks, watch glass, dish., filter paper, funnel, distilled water, UV spectrometer

Chemicals Required: $NiCl_2 \cdot 6H_2O$, aqueous ammonia, ammonium chloride, Murexide indicator, 0.05M EDTA solution, 1N H_2SO_4

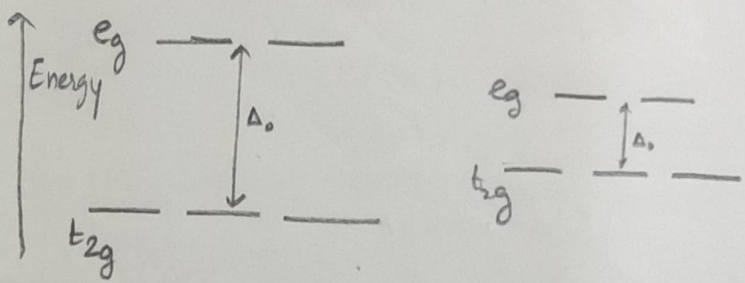
Principle: An arrangement of ligands according to their increasing ability to split d-orbitals is termed as the spectrochemical series. This field is quantified using the crystal field splitting parameter (Δ) which is determined experimentally.

(Spectrochemical series)

Weak field $I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < C_2O_4^{2-} < H_2O$

$< NCS^- < CH_3CN <$ ~~en~~ $< bipy < phen < NO_2^- < PPh_3 < CN^- \cong CO$ Strong field

$< NH_3 < en$

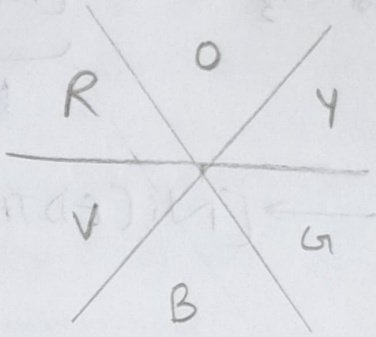


d-orbital splitting for an octahedral geometry

Strong field Weak field

Now this Δ_o can be related to colour of a complex as more the energy gap between two levels, more the energy required by e^- to jump to higher level ($t_{2g} \rightarrow eg$), so for strong field ligands ~~higher~~ frequency photons will be absorbed and correspondingly low frequency photons will be transmitted which will show their colour. and similarly low frequency photons will be absorbed & high frequency photons will be transmitted in case of weak field ligand.

As colour shown by a compound is complementary to what colour range of frequency it has absorbed, generally. It can be related as



complementary colours wheel.

VBGYOR is from VIBGYOR

In our experiment, we will synthesize the $[Ni(NH_3)_6]Cl_2$ from $NiCl_2 \cdot 6H_2O$. As we know in spectrochemical series H_2O is weaker ligand than NH_3, so NH_3 can replace H_2O to produce more stable complex.

Now, e^- transition from ($t_{2g} \rightarrow e_g$) levels depends on ligand strength, so NH_3 will cause more splitting than H_2O. so requires shorter wavelength of light, so it has blue color while H_2O complex is green in color.

Then after preparing $[Ni(NH_3)_6]Cl_2$ from $[Ni(H_2O)_6]Cl_2$ we will first cool it so that crystal precipitates & then after filtering & drying, we obtain crystals.

For estimation using titration with EDTA, as EDTA is stronger ligand than NH_3, it can replace NH_3 and forms stable complex which also has chelation, Here we use Murexide indicator which firstly binds to Ni^{+2} and after titration with EDTA, it is set free, so a colour change is observed.

(light green → bluish violet)

Estimation can also be done by UV spectroscopy for different Nickel solutions of known and our unknown concentrations. at 395nm using Beer-Lambert law

$$A = \varepsilon \cdot C \cdot l$$

A → Absorbance
ε → molar absorption coefficient
C → concentration
l → path length.

Reactions:

1) $\underbrace{[Ni(H_2O)_6]^{2+}}_{\text{green}} + 6NH_3 \longrightarrow \underbrace{[Ni(NH_3)_6]^{2+}}_{\text{blue}} + 6H_2O$

2) $Ni^{+2} + EDTA^{4-} \longrightarrow [Ni(EDTA)]^{2-}$

Procedure:

(A) Preparation of Hexamminenickel (II) chloride

1) Take 10ml of nickel chloride hexahydrate (contains 6g of $NiCl_2$) in a 250ml beaker using measuring cylinder

2) ~~Add~~ Take 12ml solution of aqueous ammonia using measuring cylinder.

3) Add ammonia solution drop wise to the solution of $NiCl_2$ with constant stirring till solution has changed color from pale green to intense violet.

4) Allow the solution to stand at room temperature for 5 minutes, cover with watch glass. Then cool it in an ice bath for 15 minutes to make precipitates.

5) We will filter this now using filter paper, while filtering some crystals may remain on side of beaker, wash them using ammonia solution and filter them also.

6) Now crystals will be at filter paper, using dropper add drops (3-5ml) of NH_3 solution, to wash crystals, on filter paper.

7) Now dry the crystals on filter paper for few hours.

8) Report the weight of dried complex.

(B) Estimation of nickel (II) by EDTA

1) Take known amount of $[Ni(NH_3)_6]Cl_2$ prepared. (1.1g taken)

2) Transfer this to a 100ml volumetric flask. Now add 50ml of 1N H_2SO_4 to dissolve it and makeup the solution to the mark with distilled water.

3) Pipette out 10ml of the complex solution in a 250ml conical flask ~~with a d~~ and dilute it with 100ml of distilled water.

4) Fill the burette with 0.05M EDTA upto zero reading.

5) Now, add 2-3 drops of murexide indicator using dropper, and 5ml NH_4Cl solution (0.5M) to the conical flask. Now add ammonia solution (7-10) drops to maintain a pH 7.

6) Mix it, so you see a light green color of the solution.

7) Titrate it with EDTA solution till the endpoint is near, while adding properly mix it, so we get a homogeneous solution.

8) Near the end point, color of solution becomes lighter & slightly blackish, so at this point we add 3ml of ammonia solution. to make solution basic slightly.

9) And now add EDTA dropwise, with constant mixing, so that we don't add additional EDTA

10) At end point a drastic colour change to bluish violet colour will appear.

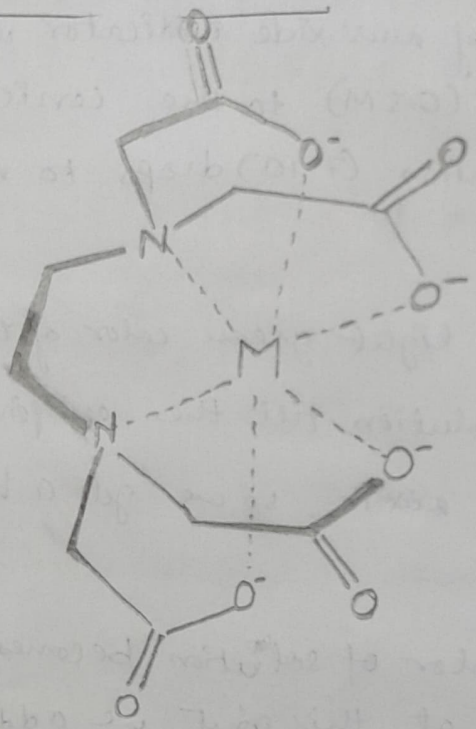
11) Repeat the titration to get concordant values

12) Calculate the amount of Ni present in the complex.

(C) Estimation of Nickel by spectrophotometry

1) Take several solutions of $[Ni(NH_3)_6]Cl_2$ of known concentration and one unknown concentration solution.
2) Measure absorbance of all solutions at 395 nm using a UV-visible spectrophotometer.
3) Plot absorbance vs mg/ml of Nickel. Determine the concentration nickel present in g/l.

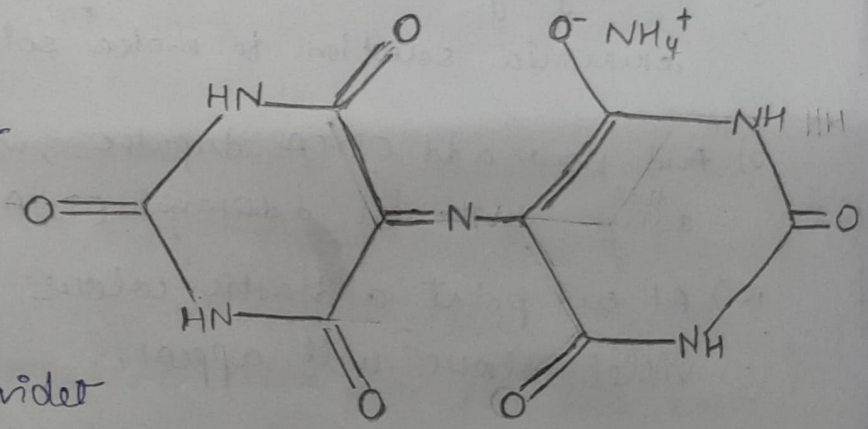
Chemical structures :



$M = Ni^{+2}$

$[Ni(EDTA)]^{2-}$

Murexide indicator



pH range : 10-11

Colour change for Ni :

Yellow-green to violet

can be represented as H_4Ind^-

$$H_4Ind^- \rightleftharpoons H_3Ind^{2-} \rightleftharpoons H_2Ind^{3-}$$

(PH<9) Reddish-violet — Violet (PH: 9-11) — Blue (PH>11)

Observations & Calculations:

Given concentration of EDTA solution = 0.05M

S.No.	Volume of EDTA used from burette
1	9.6 ml
2	9.7 ml
3	9.7 ml

1 mole of Ni reacts with 1 mole of EDTA to form Ni-EDTA complex.

Moles of Ni = Moles of EDTA

$M_1V_1 = M_2V_2$

Molarity (Ni) × 10 ml = (0.05 M) × (9.7 ml)

Molarity of Ni = 0.0485 M

Thus, the solution contains 0.0485 moles/liter of Nickel

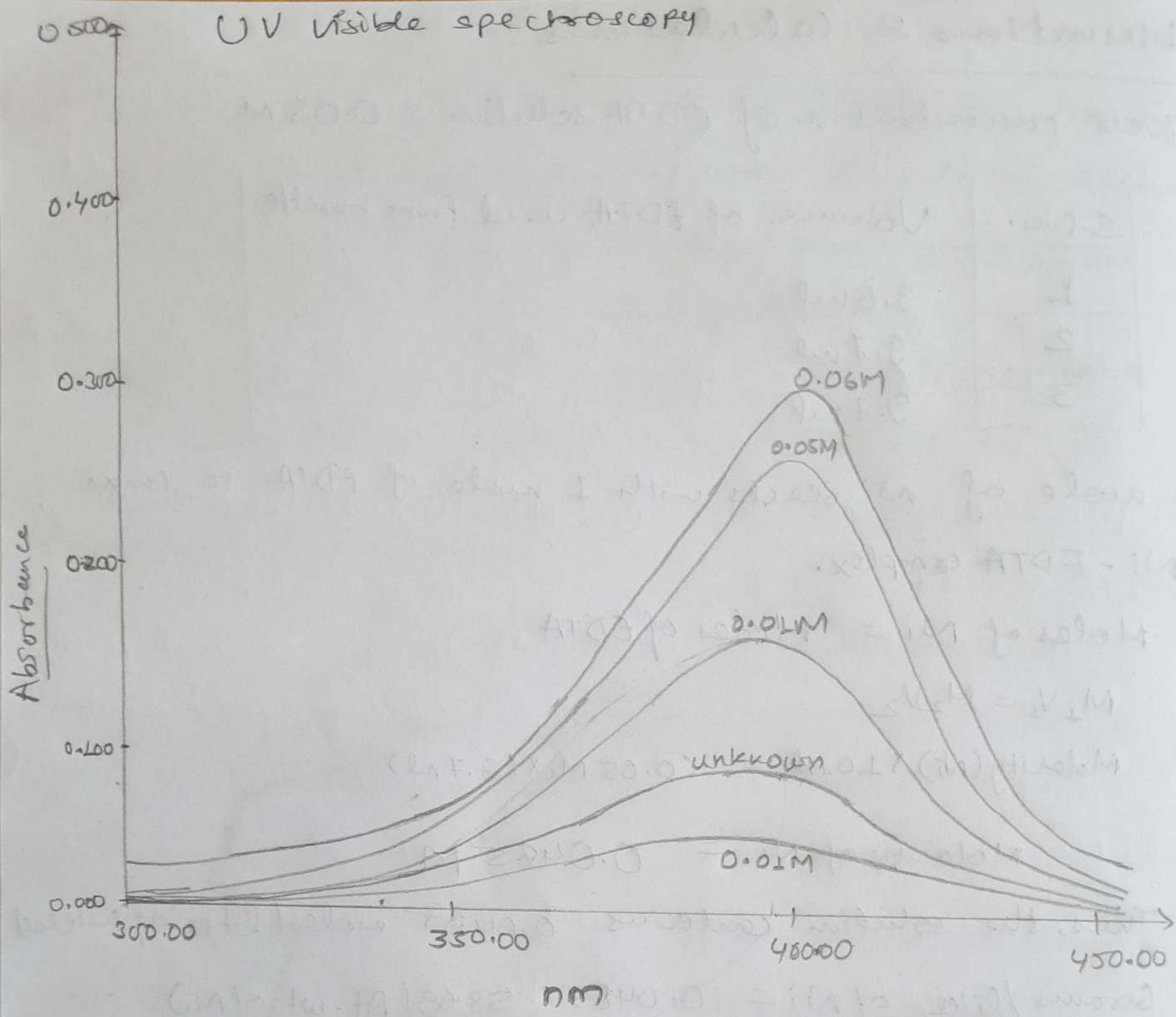
Grams/liter of Ni = 0.0485 × 58.69 (At. wt. of Ni)

= 2.85 g/l

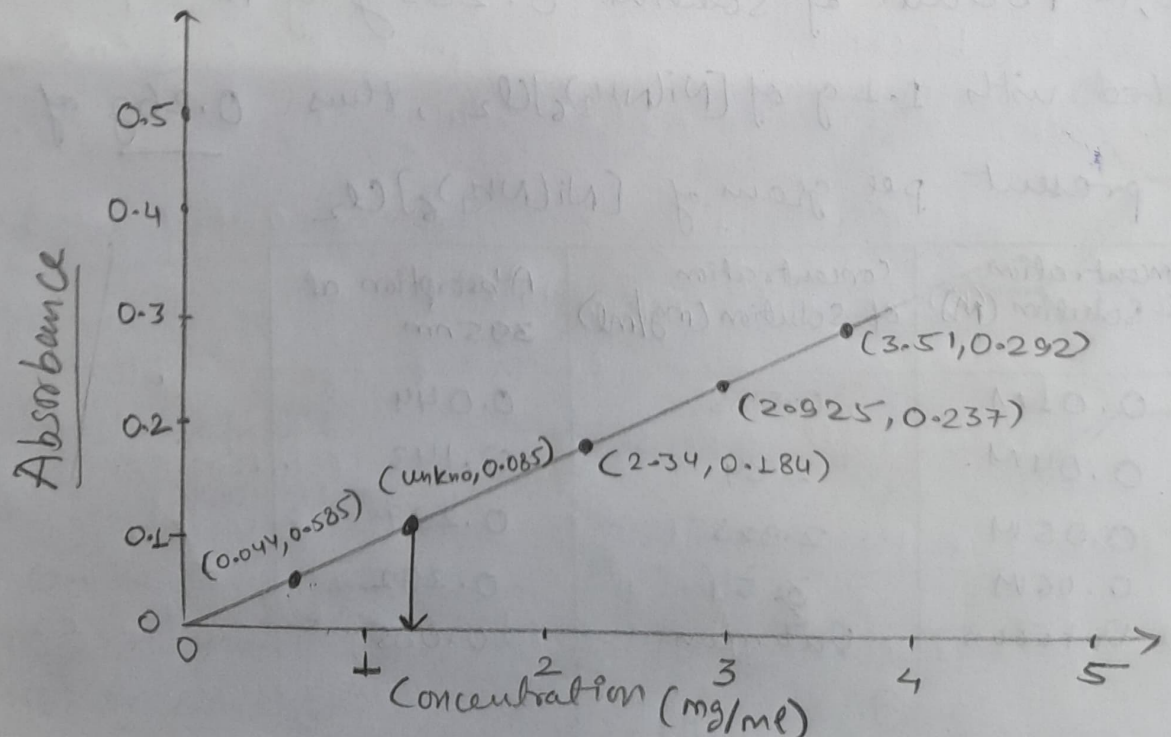
- Hence, in 100 ml of solution 0.285 g of Ni is present.
- We started with 1.1 g of $[Ni(NH_3)_6]Cl_2$, thus 0.26 g of Ni is present per gram of $[Ni(NH_3)_6]Cl_2$

S.No.	Concentration of Solution (M)	Concentration of Solution (mg/ml)	Absorption at 395 nm
1	0.01M	0.585	0.044
2	0.04M	2.34	0.143
3	0.05M	2.925	0.237
4	0.06M	3.51	0.292
5	Unknown	Unknown	0.085

UV visible spectroscopy



Absorbance plots for Nickel solutions.



The absorption of light is described by Beer-Lambert law $\boxed{A = \varepsilon . c . l}$

Using the absorbance vs concentration plot, concentration of unknown solution can be obtained.

Concentration for an absorbance of 0.085 corresponds to the value of 1.13 on the X axis $\left(x = \frac{0.085}{\left(\frac{0.044}{0.585}\right)} = 1.13 \right)$

Concentration of unknown solution = 1.13 g/ml

= 0.019M

Results: 1) $[Ni(NH_3)_6]Cl_2$ was synthesized from $(Ni(H_2O)_6)Cl_2$

2) Obtained compound was then used to estimate the amount of Nickel present

3) Amount of Nickel present: 0.26g of Ni per gram of $[Ni(NH_3)_6]Cl_2$

4) Concentration of a given solution was determined using solution of known conc with the help of UV spectroscopy

5) Concentration of unknown solution = 0.019M

Precautions: 1) Acids must be handled carefully,

2) Use of NH_3 is done with care. Inhalation of NH_3 leads to headache and faintness

3) Used cleaned burette and other cleaned equipments.