

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

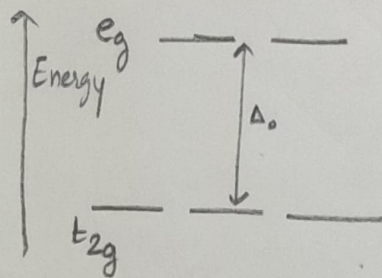
Chemicals Required: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, aqueous ammonia, ammonium chloride, Murexide indicator, 0.05M EDTA solution, $1\text{N H}_2\text{SO}_4$

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.

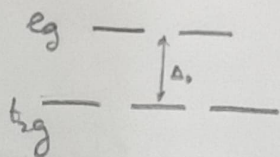
(Spectrochemical series)

Weak field $\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O}$

$\text{CN}^- < \text{CH}_3\text{CN} < \text{NH}_3 < \text{en} < \text{bipy} < \text{phen} < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$ Strong field



Strong field

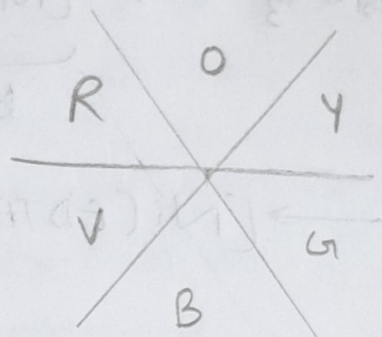


Weak field

d-orbital splitting for an octahedral geometry

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 ($t_{2g} \rightarrow e_g$), 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 colour wheel.

VBG YOR is from VIBGYOR

In our experiment, we will synthesize the $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. 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 $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ from $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ 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 ~~ED~~ titration with EDTA, it is set free, so a colour change is observed.
(light green \rightarrow bluish violet)

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

$$A = \epsilon \cdot C \cdot l$$

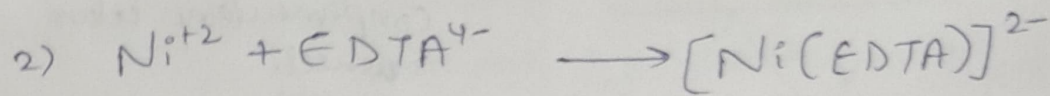
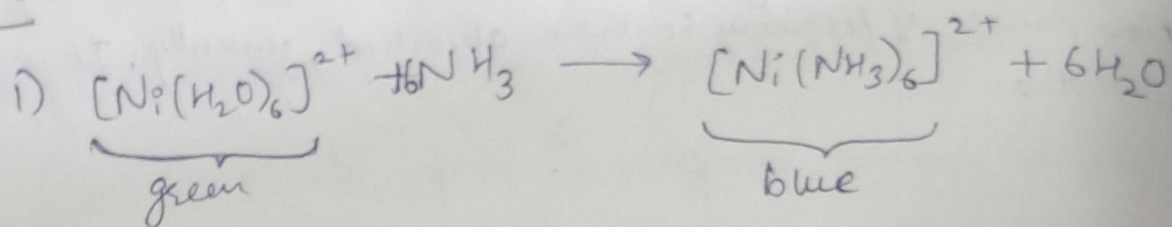
$A \rightarrow$ Absorbance

$\epsilon \rightarrow$ molar absorption coefficient

$C \rightarrow$ concentration

$l \rightarrow$ path length.

Reactions:



Procedure:

(A) Preparation of Hexammine nickel(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.

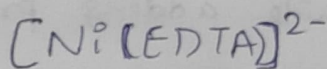
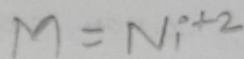
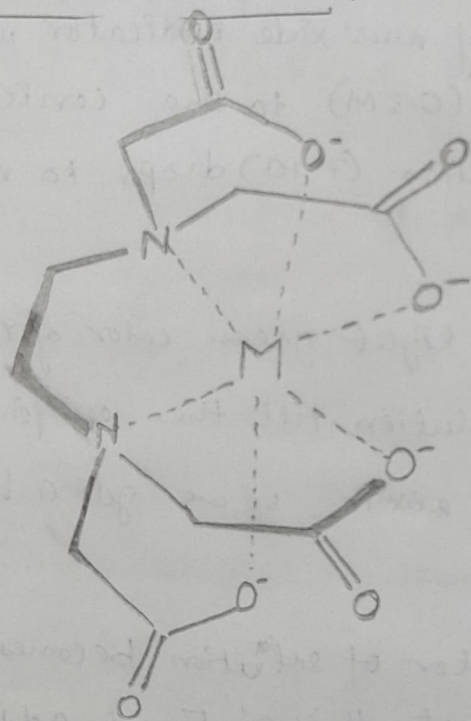
(B) Estimation of nickel (II) by EDTA

- 1) Take known amount of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ prepared. (1.6g taken)
- 2) transfer this to a 100ml volumetric flask. Now add 50ml of 1N H_2SO_4 to dissolve it and make up the solution to the mark with distilled water.
- 3) Pipette out 10ml of the complex solution in a 250ml conical flask ~~with a~~ and dilute it with 10ml 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, add 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.
^{that} 20 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 $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ 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 $\mu\text{g/ml}$ of Nickel. Determine the concentration nickel present in g/l.

Chemical structures:

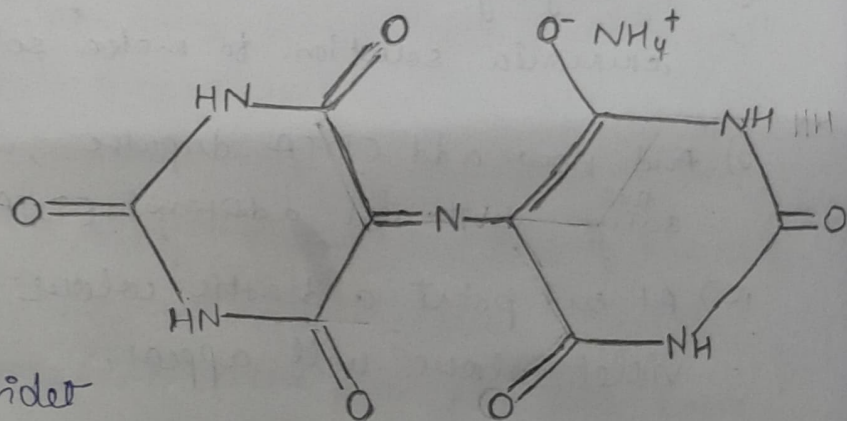


Murexide indicator

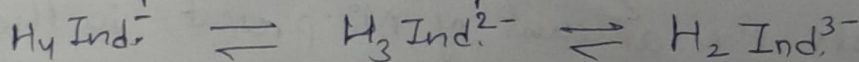
pH range: 9-11

Colour change for Ni^{2+} :

Yellow-green to violet



can be represented as H_4Ind^-



(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	9.6ml
2	9.7ml
3	9.7ml

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

Moles of Ni = Moles of EDTA

$$M_1 V_1 = M_2 V_2$$

$$\text{Molarity (Ni)} \times 10\text{ml} = (0.05\text{M}) \times (9.7\text{ml})$$

$$\text{Molarity of Ni} = 0.0485\text{M}$$

Thus, the solution contains 0.0485 moles/liter of Nickel

$$\text{Grams/liter of Ni} = 0.0485 \times 58.69 (\text{At. wt. of Ni})$$

$$= \underline{2.85\text{g/l}}$$

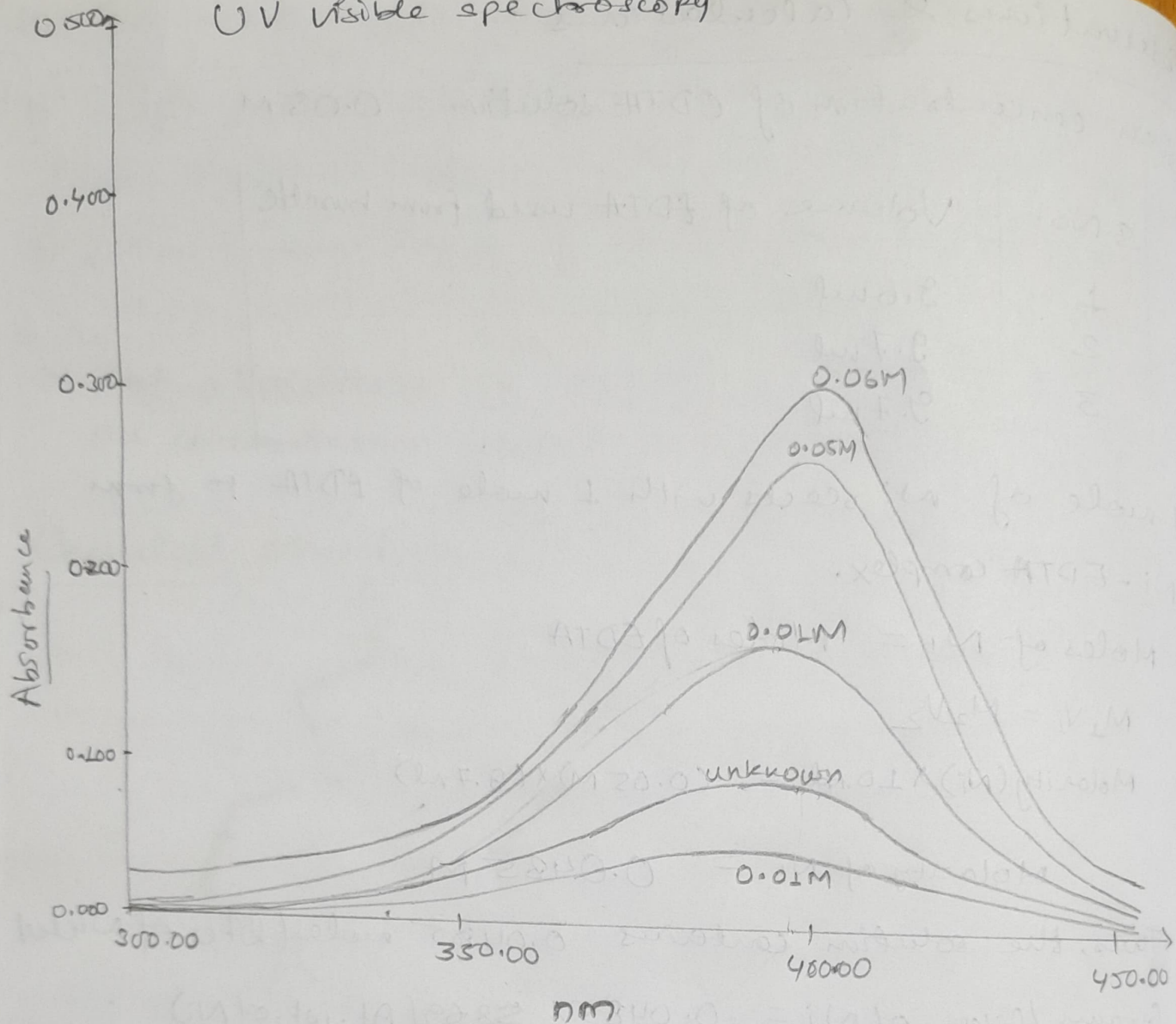
• Hence, in 100ml of solution, 0.285g of Ni is present.

• We started with 1.1g of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$, thus 0.26g of

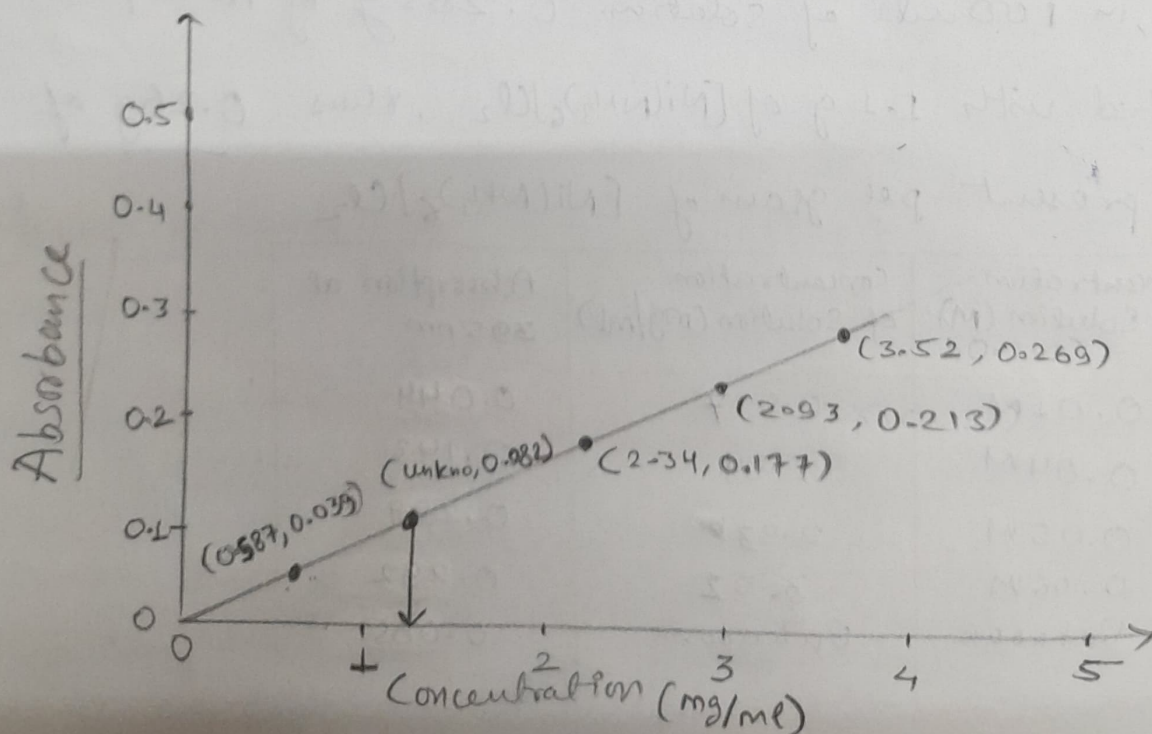
Ni is present per gram of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$

S.No.	Concentration of Solution (M)	Concentration of Solution (mg/ml)	Absorption at 395nm
1	0.01M	0.587	0.039
2	0.04M	2.34	0.177
3	0.05M	2.93	0.213
4	0.06M	3.52	0.269
5	Unknown	Unknown	0.082

UV Visible spectroscopy



Absorbance plots for Nickel solutions.



The absorption of light is described by Beer-Lambert law

$$A = \epsilon \cdot c \cdot l$$

(Absorbance & concentration)

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

Concentration for an absorbance of 0.082 corresponds to the value of 1.23 on the X-axis ($x = \frac{0.082}{\left(\frac{0.021}{1.23}\right)}$) (by $x = \frac{y}{m}$)

$$\text{Concentration of unknown solution} = 1.23 \text{ g/ml} \\ = 0.021 \text{ M}$$

Results: 1) $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ was synthesized from $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$

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 $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$

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

5) Concentration of unknown solution = 0.021 M

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.