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Lab Manual for M.Sc. Chemistry

(For both I & II year)

PRACTICAL INORGANIC CHEMISTRY

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INORGANIC CHEMISTRY

PRACTICAL - I

A. COLORIMETRIC ANALYSIS

Introduction

Colourimetric analysis is based on the variation of the colour of the system with change in concentration of the analyte. The colour is usually due to the formation of a coloured compound by addition of an appropriate reagent or it may be inherent in the desired constituent itself. The intensity of colour may then be compared with that obtained by treating a known amount of the substance in the same manner.

Colorimetry is concerned with the determination of the concentration of a substance by measuring the relative absorption of light with respect to a known concentration of substance. In visual colorimetry natural or artificial white light is generally used as a light source and the determination is made with a simple instrument called colorimeter. The main advantage of colorimetric method is that it provides a simple means for determining minute quantities of substances (1 or 2%).

Principle

When light falls upon a homogeneous medium, a portion of the incident beam is reflected, a portion is absorbed within the medium, and the remainder is transmitted. When a monochromatic light passes through a solution (coloured or transparent) the intensity of the transmitted light decreases exponentially as the thickness or concentration of the absorbing medium increases arithmetically. This is known as Beer - Lambert's law and may be written in the form :

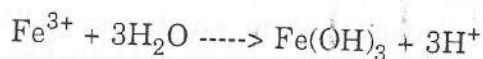
$$I_t = I_0 10^{-\epsilon Cl} \text{ or } \log I_0/I_t = \epsilon Cl$$

ϵ	=	Molar extinction coefficient (molar absorptivity)
C	=	Concentration (moles/litres)
l	=	length or thickness of the medium (cm)

ESTIMATION OF IRON

Principle

A convenient and sensitive method for the colorimetric determination of iron is based on the intense red colouration which ammonium or potassium thiocyanate gives with a solution of ferric salt (Ferrous salts do not react). The solution containing iron must be strongly acidic to suppress the hydrolysis.



and H_2SO_4 is not recommended, because sulphate ions may form complex with Iron (III) ions (0.5 M HCl or HNO_3 is recommended).

The red colouration fades slowly on account of spontaneous decomposition of the ferric thiocyanate. This method is satisfactory in many cases but in the presence of phosphate, fluorides and certain organic acids, which form complexes with Iron (III), the development of colour is seriously affected. Metals which are precipitated by ammonium thiocyanate and those which give a coloured solution with this reagent interfere in the determination. In such cases iron must first be separated with a slight excess of ammonia solution and dissolve the $\text{Fe}(\text{OH})_3$ in dilute HCl.

Ferric iron reacts with thiocyanate to give a series of intensely red coloured complexes, which remain in solution. Ferrous iron does not react. Depending upon the thiocyanate concentration a series of complexes can be obtained. These complexes are red and can be formulated as $[\text{Fe}(\text{SCN})_n]^{3-n}$, where $n = 1$ to 6. At low thiocyanate concentration (0.1 M) the predominant coloured species is $[\text{Fe}(\text{SCN})]^{2+}$, and at very high thiocyanate concentration it is $[\text{Fe}(\text{SCN})_6]^{3-}$. In colorimetric determination a large excess of thiocyanate should be used as it increases the intensity and also the stability of the colour (complex).

Reagents

1. Ferric ammonium sulphate

Dissolve 0.7022 g of A.R. Ferrous ammonium sulphate in 100 ml of water add 5 ml of 1:2 HNO_3 (or 1:1 HCl) and add cautiously a dilute solution of potassium permanganate (2g / litre) until a slight pink colouration remains after stirring well. Dilute to 1 litre and mix thoroughly. (1 ml contains 0.1 mg of Fe).

(OR)

Dissolve 0.432 of ferric ammonium sulphate in water add 10 ml of conc. HCl (or HNO_3) and dilute to 1 litre. (1 ml contains 0.05 mg of iron)

2. Potassium thiocyanate

Dissolve 20 g of AR potassium thiocyanate in 100 ml water. (2M)

Procedure

Dissolve a weighed portion of the substance in which the amount of iron is to be determined in a suitable acid and evaporate nearly to dryness. Dilute slightly with water, oxidise iron to ferric state with dilute KMnO_4 and make up to 250 ml (or) make up the given unknown solution to 250 ml.

Measure with a pipette 5 ml of unknown iron solution into a Nessler tube, add 2 ml of 4 M HCl (or HNO_3) and dilute to 25 ml mark. Add 5 ml of ammonium thiocyanate solution mix and dilute to 50 ml mark. Into four other Nessler tubes add 1,2,3,4 ml of standard iron solution and 2 ml of 4 M HCl (or HNO_3) dilute to 25 ml

and add 5 ml ammonium thiocyanate solution to each tube, mix and compare the colours with the unknown after diluting to 50 ml mark and fix the range (say between 4 and 5 ml).

Into four other Nessler's tubes pipette out the observed volumes of the standard solution (say 4.2, 4.4, 4.6, 4.8 ml) add 2 ml of 4 M HCl dilute to 25 ml mark and add 5 ml of ammonium thiocyanate mix and dilute to 50 ml mark. The depth of the colour in one of the tubes match exactly with that of unknown.

Better results are obtained with a photoelectric colorimeter. Use a filter showing maximum transmission at or near 480 nm (blue-green filter) and determine the absorbance of the unknown solution. Prepare a set of standard solutions with 1 to 5 ml of iron (Fe^{3+}), add 2 ml of 4 M HCl and 5 ml of ammonium thiocyanate and make upto a known volume (Say 50 or 100 ml in an SMF). From the absorbance of these solutions construct a calibration graph, from which the amount of iron in the unknown solute can be calculated.

2. ESTIMATION OF NICKEL

Principle

When dimethyl glyoxime is added to an alkaline solution of Nickel (II) salt which has been treated with an oxidising agent (such as bromine), a red colouration is obtained. The red soluble complex contains nickel in a higher valency state (may be Ni(III) or Ni(IV)). The nickel complex formed absorbs at about 445 nm provided absorbance reading are taken within 10 minutes of mixing. The DMG - Nickel complex formed by this procedure is different from Ni(II) - DMG complex which is soluble in chloroform and insoluble in water.

Reagents

1. Standard Nickel (II) solution

Weigh 0.673 g of AR Nickel ammonium sulphate in water and dilute to 1 litre. This solution contains 0.1 mg/ml of Nickel. This solution is further diluted to a basis of 0.01 mg/ml of Nickel.

2. DMG Solution - Dissolve 1 g of DMG in 100 ml of ethanol.
3. Saturated bromine water and
4. Ammonia.

Procedure

Transfer 1 to 5 ml of Standard Nickel solution containing 0.01 mg/ml of Ni(II) solution to a series of 50 ml Volumetric flasks, add 20 ml of water followed by 1 ml of saturated bromine water. Then add 2 ml of conc. ammonia solution. Add 1 ml of 1% DMG and dilute to 50 ml and allow it to stand for 5 minutes. Measure the absorbance at 445 nm against the blank and construct a calibration graph.

The given unknown solution is made upto 250 ml. From this 5 or 10 ml is pipetted out into 50 ml standard flask and develop the colour following the procedure outlined above. (colour comparison can also be done using Nessler's reagent)

Note : The final Nickel concentration should not exceed 0.6 mg/100 ml because a precipitate may form above this concentration. For calibration purpose use 0.5 to 4 ml of Nickel (II) solution containing 0.01 mg/ml. For giving unknown solution to students, prepare a stock solution containing 1 mg/ml of Nickel by dissolving 6.73 g of Nickel ammonium sulphate in 1 litre. Each student may be given 5-10 ml of solution and can be asked to dilute to 250 ml, from which 0.5 to 4 ml can be used for colour development. If precipitate occurs the solution may be diluted further. From the calibration graph the amount of Nickel in the unknown solution can be calculated.

3. ESTIMATION OF MANGANESE

Principle

Manganese is determined colorimetrically by using manganous sulphate and potassium periodate which is a oxidising agent. The absorbance is calculated from their transmittance for various concentration of manganese. Calibration graph is drawn and unknown is found from the graph.

Procedure

About 0.1 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ is weighed and made upto 250 ml in a standard flask. From the standard solution 20 ml is pipetted out into a conical flask, to this 5 ml of syropy phosphoric acid is added and approximately 0.5 g of potassium periodate is added and boiled for 5 minutes. It is kept hot for 10 mts, cooled and then it is made upto 100 ml in a standard flask. Various concentration are pipetted out into separate 100 ml standard flasks and made upto the mark and corresponding transmittance or absorbance at 545 nm is measured by using colorimeter. Calibration graph is drawn.

Th given unknown solution is made upto 100 ml in a standard flask and 20 ml of this solution is pipetted out into a conical flask. The above procedure is repeated for oxidation. The coloured solution is made upto 100 ml and from this 20 ml of solution is pipetted out and diluted to 100 ml, then the absorption is measured for unknown concentration the amount of manganese is calculated from the calibration graph.

4. ESTIMATION OF COPPER

Potassium ferrocyanide as hitherto been the usual reagent for the colorimetric estimation of copper, but sodium diethyldithiocarbamate is a more sensitive reagent for copper and gives a colour which is easily matched. One part of copper in 50,000,000 of solution gives a definite orange yellow colouration, and the colour is

produced in acid, alkaline and neutral solution. The colour produced is stable for several hours.

Reagents required

1. Standard copper solution

Dissolve 0.393 g of pure crystalline copper sulphate, make up the solution to 1 litre. Dissolve 25 ml of this to 250 ml. 1 ml of this solution contains 0.1 mg of copper.

2. Standard diethyldithiocarbamate - Dissolve 0.1 g in 100 ml water.

Procedure

If iron is present, add 1 ml of concentrated nitric acid to a measured volume of the solution to be determined, and evaporate to a small bulk. Precipitate the iron by adding a slight excess of ammonia, filter and wash. Dissolve the ferric hydroxide in dilute nitric acid, reprecipitate with ammonia, filter and wash. Combine the two filtrates and dilute to a known volume.

A suitable depth of colour for matching is obtained with about 0.05 mg of copper in the final volume of Nessler's tube.

Prepare standard solution as follows

Measure 5 ml of the standard copper solution into a 50 ml Nessler's tube, add 20 ml of dilute ammonia, dilute to the mark, add 10 ml of the reagent, mix and dilute to the mark. The remainder of the process is carried out in an analogous manner to that described under iron.

B. PREPARATION OF COMPLEXES

1. Potassium trisoxalatoaluminate(III) hydrate

Chemicals required

Commercial Aluminium turnings (Dural alloy), Potassium hydroxide, Oxalic acid (dihydrate), ethanol, Glass wool, filter paper.

Procedure

Weigh 1 g of commercial aluminium turnings and transfer into a 200 ml beaker. Cover the metal with 10 ml of warm water. Add 30 ml of potassium hydroxide solution in portions, as the vigorous effervescence subsides. Heat the contents to the boiling temperature to dissolve the aluminium completely. Filter the solution through a small plug of glass wool inserted into the base of the funnel. The filtrate may contain finely divided particles which can be removed later. Add 10 ml of water to the filtrate and then heat the solution to the boiling temperature. Weigh out 14 g of oxalic acid and add it in portions to the hot solution until the precipitate of hydrated alumina formed at first is just redissolved on continued boiling [Avoid excess of acid].

Filter the neutralised solution by suction through filter paper from the final traces of residue. Cool the filtrate to room temperature and then add 50 ml of ethanol. Continue the cooling in running water or ice. The complex separates out as small colourless prisms. [Occasionally a concentrated aqueous solution may separate as second layer. Crystallisation can be induced by vigorous shaking.] Filter the complex with filter paper, wash the crystal first with an equimolar mixture of ethanol and water and finally with ethanol. Dry in air at room temperature. Yield \approx 11 g.

2. Preparation of trithiourea copper (I) sulphate

Chemicals Required

Copper sulphate	- 2 g
Thiourea	- 1.5 g

Procedure

2.5 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 15 ml water was mixed with the solution of 15 ml thiourea (1.5 g). The mixture is cooled on a ice bath. The products of mixture appears as white crystals.

Recrystallise the product by dissolving in it into dilute thiourea solution containing few drops of 1 M H_2SO_4 . The solution is heated to a max of 75°C to dissolve the product and cooled. The filtered crystals on a funnel was washed with 5 ml of water and then with 5 ml of alcohol. The crystals are dried. Yield 2.5 g.

3. Potassium trisoxalatochromate (III) trihydrate

Chemicals required :

Potassium dichromate, Oxalic acid (dihydrate), Potassium oxalate, ethanol.

Procedure

Weigh 9 g of oxalic acid (dihydrate) and transfer it to 200 ml beaker. Add 20 ml of water and warm the solution. To this add in portions 3 g of potassium dichromate. Allow the vigorous reaction to subside and then heat the solution to boiling. To the boiling solution add 3.5 g of Potassium oxalate. After two minutes of boiling, cool the solution to room temperature and then add 35 ml of ethanol. Continue the cooling. Blue green crystals of the complex will separate out from an almost black solution. Filter the crystals through a filter paper, wash first with an equivolume mixture of ethanol and water and finally with pure ethanol. Dry the crystals at room temperature in air. Yield of the complex \approx 6 g.

4. Sodium cuprousthioulsulphate ✓

Chemicals Required

✓ Cupric sulphate, sodium thiosulphate and acetone. ✓

Procedure

Dissolve (i) 10 g of cupric crystal in 50 ml of warm water, (ii) 18 g of sodium thiosulphate crystals in 30 ml of warm water. Adjust the temperature of each solution to about 40°C and then pour the solution of thiosulphate into the well stirred cupric solution. After a short time, the crystalline, bright yellow complex thiosulphate begins to separate and is fully deposited in about an hour. It is then filtered off by the use of the filter pump, and the solid thoroughly washed on the filter with cold water, which is finally displaced by acetone to facilitate drying the product at a temperature not exceeding 50°C , Yield \approx 7.6 g.

5. Tetramminecopper (II) sulphate

Chemicals Required

Cupric sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentrated ammonia solution and alcohol.

Procedure

Dissolve the 10 g of copper sulphate in 50 cc of water and filter it if necessary. Add the conc. ammonia solution to the solution of copper sulphate taken in a beaker drop by drop, until the precipitate at first formed dissolves in the excess of ammonia, giving a blue solution. Then add another 10 ml of ammonia, followed by alcohol, until a permanent blue precipitate begins to form. Warm the solution on a water bath,

adding more alcohol, if this can be done without causing precipitation, then allow the clear, deep blue solution to cool and to stand at room temperature as long as crystallisation continues. Drain the solution from the crystals and dry the crystals on filter paper in the air. Do not, however, leave them exposed longer than necessary since they easily lose ammonia. Preserve the crystals in a tightly stoppered bottle. Yield 7.5 g.

6. Preparation of potassium tetrachlorocuprate(II) $K_2[CuCl_4]$

Weigh 10 g of $CuCl_2$ and transfer into a 200 ml RB flask. Add 20 ml of thionyl chloride until all the $CuCl_2$ dissolves. Fit a reflux condenser. When the evolution of SO_2 ceased reflux under nitrogen for about 2 hours. Distill off excess thionyl chloride under low pressure using water filter add 10 ml acetic anhydride to the residue. Filter and wash the residue with small portions of acetic anhydride. Place in an ampoule and dry in a vacuum desiccator. Yield 7.2 g.

$[CuCl_4]^{2-}$

C. SEPARATION OF MIXTURE OF TWO METAL IONS BY PAPER CHROMATOGRAPHY

Principle

Capillary analysis is the precursor of present day paper chromatography. It was shown that when a solution was allowed to rise through paper by capillary action, the solvent migrated faster than the solute. The solutes present in the solution were retained to different extent by filter paper and the relative distance reached by different solutes were characteristic of the solutes.

The filter paper used as absorbent is a very high purity sample of cellulose. Cellulose molecule is a polymeric structure made up of several thousand glucose units linked through oxygen. Three hydroxyl groups are available on each glucose residue and there are potential aldehyde groups on the ends of chain. There is also very low mineral content which is chemically active to some extent. The cellulose contains hydroxyl, carboxyl, aldehyde and ketone functional groups and is highly polar. It has great affinity for water and other polar solvents and holds them strongly through the formation of hydrogen bonds. Mechanical and chemical treatment shortens the naturally long glucose chains and contributes to the capillary adsorption properties of the cellulose. The diffusion of the solution through filter paper is due to capillary and adsorption phenomena. Relatively large interstitial spaces between the cellulose fibres are responsible for the rate of diffusion. Smaller capillaries within the individual fibres expose a large surface area which is favourable to increase absorption of solutes. The cellulose water complex acts as stationary phase and hence the separation of solutes is by partition mechanism. Nevertheless, adsorption process also play a definite but minor role in the differential migration of solutes in the paper.

Three types of techniques are available for carrying out paper chromatographic experiments, namely ascending, descending and radial. In the ascending technique, the solvent flows upward through filter paper by capillary action. As the solvent is flowing against the pull of gravity, there is practical limit to the height of the solvent can rise. In the descending technique, the problem lies with ascending technique especially the flow of solvent was overcome by letting the solvent downwards through a paper. In radial chromatography, the solvent is allowed to flow radially in a plane.

The position of the various solute zones after the chromatogram is developed are measured relative to the position of the solvent front. Relative migration of the solutes are expressed as R_f values.

$$R_f = \frac{\text{Distance moved by solute}}{\text{Distance moved by solvent}}$$

The measurement is made by measuring the distances from the starting point (centre of initial mixed zone) to the developer front and the centre density of each

zone. For locating the solute zone on the paper any one of the following techniques can be used.

1. The chromatogram can be exposed to UV radiation.
2. Spraying with reagent which will give colour.

I. Separation of Nickel and Cobalt and determination of R_f values

Reagents

1. Weigh 500 mg of Nickel ammonium sulphate and dissolve in 100 ml of water.
2. Weigh 400 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and dissolve in 100 ml of 2 M hydrochloric acid. [The solution contains 1 mg of Co^{2+}/ml].
3. Stock solution of the mixture : Mix 10 ml Ni^{2+} solution and 10ml Co^{2+} solution and this solution is used as sample solution.
4. Acetone. HCl solvent mixture : Mix 43.5 ml of AR acetone, 4 ml of concentrated hydrochloric acid and 2.5 ml of water.
5. Rubeanic acid : Prepare a 0.1 M solution of rubeanic acid in ethanol.

Procedure

Place 10 - 15 ml of the solvent mixture in a **petridish** into a clean desiccator for equilibrating the chromatographic chamber. Cut the filter paper in circular form similar in size to chromatographic plates. Using capillary, place a small drop of the sample mixture at the centre of the filter paper. Care must be exercised to prevent the spreading of the spot. After loading the sample into a small area, dry the filter paper. After the spot is dried, introduce a wick at the centre of paper with the help of needle and twine. The filter paper with the wick is placed in between the plates and then on the petridish inside the desiccator. Allow the solvent to flow through the paper. When the solvent front reaches more or less the edge of the paper (0.5 cm less than the radius) remove the filter paper and dry the solvent. Mark the solvent front with a pencil. Expose the dried paper to ammonia vapours to neutralise the acid. Then spray the paper with rubeanic acid and dry. Cobalt will give yellowish orange band and nickel will give a blue purple band. Calculate the R_f values of Cobalt and nickel from the distance moved by the solute and solvent.

II. Separation of Copper and Cobalt and determination of R_f Values.

Chemicals and apparatus : Copper sulphate, cobaltous chloride, acetone, ethyl acetate, hydrochloric acid and rubeanic acid.

Reagents

- (1) Weigh 440 mg of copper sulphate and dissolve in 100 ml of water.
- (2) Weigh 400mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and dissolve in 100 ml of water.
- (3) Sample solution : Mix 10 ml each of the neutral solutions to get 20 ml. (each solution contains 1 mg of each metal ion).
- (4) Solvent : Prepare a mixture of acetone, ethylacetate and 6 M HCl in the ratio 9:9:2 by volume from AR reagents.
- (5) Spraying reagents : Prepare 0.1 % solution of rubeanic acid in ethanol.

Procedure

As described for the previous experiment. Cobalt gives a yellow orange band and copper gives an Olive green band. Calculate the R_f values.

INORGANIC CHEMISTRY

PRACTICAL - II

A. ANALYSIS OF ORES

1. ANALYSIS OF LIMESTONE OR DOLOMITE

Limestone consist essentially of calcium carbonate, but may contain also some magnesium carbonate. If the proportion of magnesium carbonate is considerable, the rock is called a dolomite. The usual minor constituents are iron, aluminum silica (either free or combined), and manganese. A careful qualitative analysis must therefore precede the quantitative analysis.

In the following description of the analysis, it is assumed that a dolomite containing magnesium and calcium carbonates with small quantities of iron, aluminum silica (or silicate), and phosphate is under examination. The results of the analysis of a rock are usually stated in terms of the constituent basic and acidic oxides, expressed as percentages. In dolomite, for example, the results are given in terms of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , CO_2 , P_2O_5 and H_2O and it is convenient to tabulate them in that order.

1. ESTIMATION OF CALCIUM AND MAGNESIUM IN DOLOMITE

Procedure

About 1 g of the ore is weighted accurately, transferred into a breaker and made into a paste with water. Dilute hydrochloric acid is added to this till the effervescence ceases and the solution becomes clean. Then the solution is boiled, cooled and made upto 250 ml in a standard flask.

Pipette out 40 ml of the solution into a beaker, dilute with water, add few drops of methyl red indicator. This is heated to 80°C and 15 ml of 3% ammonium oxalate is added slowly with constant stirring. Ammonium hydroxide is added till the solution turned yellow in colour. The calcium oxalate is digested on a boiling water bath for about half an hour and tested for the completion of precipitation. It is filtered through a whatman filter paper and the filtrate containing magnesium is collected. The precipitate is washed with dilute ammonia solution.

Estimation of Calcium

The precipitate of calcium oxalate is dissolved in hot sulphuric acid and the hot solution is titrated against Std. KMnO_4 . A duplicate experiment is conducted.

Estimation of Magnesium

Reagent

1. EDTA solution 0.1 M

Dissolve 3.723 g of AR disodium dihydrogen ethylenediamine tetra-acetate dihydrate in water and dilute to 1 litre in a volumetric flask with distilled / deionised water.

2. Eriochrome Black T indicator

Dissolve 0.2 g of the dyestuff in 15 ml of triethanolamine and 5 ml of absolute ethanol.

Procedure

The filtrate is made upto 100 ml with distilled water. 20 ml of the solution is pipetted into a conical flask and add 2 ml of the buffer solution (pH = 10) and 3-4 drops of Erio T indicator. Titrate with 0.1 M EDTA until the colour changes from red to pure blue. The last trace of reddish shade should disappear at the end point. Complex formation does not takes place instantaneously, titration should therefore be conducted slowly near the end point.

1 ml of 0.1 M EDTA = 2.432 mg of Mg.

2. DETERMINATION OF PERCENTAGE OF MnO_2 IN PYROLUSITE

Principle

MnO_2 occurs in nature as the mineral pyrolusite. This may be analysed treating the ore with a excess of an acidified solution of reducing agent such as FeSO_4 , $\text{Na}_2\text{C}_2\text{O}_4$ or As_2O_3



The excess of reducing agent is determined by titration with standard KMnO_4 solution. The disadvantage of using FeSO_4 solution is that the operation must be carried out in an atmosphere free from air in order to prevent aerial oxidation of the ferrous sulphate. Both sodium oxalate and arsenious oxide which are primary standards and are stable in air, more convenient. Arsenious oxide is somewhat more trust worthy in this determination than sodium oxalate because oxalic acid

decomposes very rapidly at higher temperature into CO and CO₂ the decomposition under ordinary circumstances is very small.

Chemicals Required

0.1 N sodium oxalate, 4 NH₂SO₄ and 0.1 N KMnO₄.

Procedure

About 0.2 g of the pyrolusite is weighed accurately and finely powdered. This is transferred into a clean conical flask and add 50 ml Na₂C₂O₄ and 50 ml of 4 N H₂SO₄ and place a short funnel in the mouth of the flask. Boil the mixture gently until no black precipitate remains. Allow to cool and the excess of oxalate is titrated against the KMnO₄. The end point is the appearance of pale pink colour. The titration is repeated for concordant values.

3. DETERMINATION OF PERCENTAGE OF LEAD IN GALENA

Principle

The constituent of galena is lead sulphide. The sulphide ion is oxidised to sulphate ion by concentrated HNO₃ and Br₂/H₂O. Lead is precipitated as lead sulphate. Dissolve the precipitate in sodium acetate solution and estimated as lead chromate by addition of K₂CrO₄ as follows.



Procedure

About 0.2 g of finely powdered galena is taken in a breaker add 10 ml of dilute HNO₃ and are allowed to stand for 10 minutes. The solution is digested on a water bath with 15 ml of concentrated HNO₃ and then evaporate to dryness. Again 10 ml of concentrated HNO₃ is added followed by little water and 10-15 drops of Br₂/H₂O. Heat with stirring for sometimes on water bath and evaporated with concentrated HNO₃ to dryness. Repeat the process thrice. The residue is boiled with 10 ml of water and 20 ml of concentrated HCl. The insoluble gangue is filtered off and wash with hot water and 10 C.C. of dilute HCl. Make the solution too 100 ml. 40 ml of the solution is taken and lead is precipitated as PbSO₄ by adding excess of Conc. H₂SO₄ to the filtrate. Impure sulphate is removed and washed with 10% H₂SO₄ to remove solid impurities and then with 50% ethanol to remove peracid. Lead sulphate is dissolved from the impurities of the residue by repeated extraction with a strong solution of ammonium acetate. Then the solution containing lead is acidified and 15 ml of 5% K₂CrO₄ is added in boiling condition. It is then digested and the precipitate is filtered through a previously weighted sintered glass crucible. Washings are done with water.

B. ALLOY ANALYSIS

1. ESTIMATION OF LEAD IN SOLDER

Principle

A mixture of stannic tin and lead ions may be complexed with excess of standard EDTA solution; the excess of EDTA may be determined by titration with standard lead nitrate solution at pH 5-6 using xylenol orange as indicator. This gives the lead and tin content of the solution. If sodium fluoride is now added, the EDTA is now displaced from its tin complex in amount equivalent to the tin (fluoride complex of stannic tin is of higher stability than its EDTA complex): liberated EDTA is titrated with standard lead nitrate solution and the tin content thus evaluated. The relationship between standard EDTA solution and the standard lead nitrate solution is established by titration with the latter at pH 5-6 in the xylenol orange indicator.

Reagents

EDTA solution, 0.2 M
Lead nitrate solution, 0.1 M
Hexamine solution
Xylenol orange indicator.

Procedure

Dissolve a weighed amount of solder (about 0.4 gm) in 10 ml of concentrated HCl and 2 ml of concentrated nitric acid; gentle warming is necessary. Boil the solution gently for about 5 minutes to expel nitrous fumes and chlorine, and allow to cool slightly, where upon some lead chloride may separate. Add 25 ml of standard 0.2 M EDTA and boil for 1 minute; the lead chloride dissolves and a clear solution is obtained. Dilute with 100 ml of water and cool dilute to 250 ml in a standard flask. Without delay pipette two or three 25 ml portions into separate conical flasks to each flask add 15 ml of hexamine solution, 100 ml of distilled water and a few drops of xylenol orange indicator. Titrate with the standard lead nitrate solution until the colour changes from yellow to red (Titre A). Now add 2 g of A.R. sodium fluoride, the solution acquires a yellow colour owing to the liberation of EDTA from its tin complex. Titrate again with the lead nitrate solution until a permanent (i.e., stable for 1 minute) red colour is obtained (Titre B). Add the titrant drop wise near the end point, a temporary pink or red colour gradually reverting to the yellow signals the approach of the end point. Repeat the above titration.

Dilute 25 ml of the standard 0.2 M EDTA solution to 250 ml in a volumetric flask. To 25 ml of diluted solution add 1 ml of concentrated HCl, 15 ml of the hexamine solution, about 100 ml of water, and a few drops of xylenol orange indicator. Titrate with standard lead nitrate solution to the yellow to red end point (Titre C).

Calculating the percentage of Tin and Lead

EDTA solution = 0.200 M

Weight of solder used = g.

Lead nitrate solution =

Titre A : mean value = 24.05 ml = 25.0 ml of 0.02 M - {Sn+Pb}/10

Titre B : mean value = 15.00 ml = {Sn /10}

Titre C : mean value = 50.15 ml = 25.0 ml of 0.02 M EDTA

percent of tin = $T_B \times N_1 \times 118.70 / W$ of the solder

The lead in the solution (L) $10 \{C - (A+B)\} = 111.00$ ml of lead nitrate solution.

percent of lead = $(L \times N_1 \times 207.21) / (1000 \times W)$

N_1 = Strength of lead nitrate solution

T_B = Titre value of B

W = Weight of the solder.

2. ESTIMATION OF COPPER AND ZINC IN BRASS

Principle

Copper is estimated iodometrically in the presence of zinc by titrating the liberated iodine against standard thio, using starch as indicator.



From this $2 \text{CuSO}_4 = \text{I}_2 = 2 \text{Na}_2\text{S}_2\text{O}_3$

Zinc is estimated after removing the copper present as copper sulphide by passing H_2S in acidic solution and it is removed by filtration. To the remaining solution 8-hydroxy quinoline is added. Zinc is precipitated as 8-hydroxyquinolate complex. It is dried and weighed.

Procedure

Weigh about 1 g of A.R. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and dissolve it in deionised water and make upto 100 ml in a standard flask. Pipette out 20 ml of CuSO_4 solution in a clean conical flask. To this solution NaOH is added and permanent precipitation of $\text{Cu}(\text{OH})_2$ is formed. Add dilute acetic acid, (1:1) until the above precipitate dissolves. 10 ml of 10% KI is added and titrated against thio solution. The colour of the solution becomes pale yellow and 2 ml of starch is added and titration is continued till the colour changes. The same procedure is repeated till the concordant values are obtained.

About 1 g of alloy is weighed and dissolved by boiling in 10 ml of concentrated nitric acid and 4 ml of water in a beaker and then add 10 ml of concentrated sulphuric acid and evaporate in a hood. Carefully add 30 ml of water. Boil the solution for 1-2 minutes and allow it to cool. With good mixing, add conc. HNO_3 dropwise until the first

dark blue colour appears. The solution smell faintly of ammonia. Add 3 ml of concentrated H_2SO_4 until the colour disappears. 2 ml of H_3PO_4 is added and the solution is made upto 250 ml.

Estimation of Copper

Pipette out 20 ml of this solution in a clean conical flask. To this solution 1 N NaOH is added dropwise until a slight permanent precipitate of cupric hydroxide is formed. Add dilute acetic acid till the above precipitate dissolved. Add 10 ml of 10% KI and titrated against standard thio solution. The colour of the solution becomes pale yellow and 2 ml of starch is added. The titration is continued till the solution becomes colourless. The procedure is repeated till concordant values are obtained.

Estimation of Zinc

Pipette out 40 ml of the solution in a clean beaker, add 5 ml conc. HCl and pass H_2S gas for about 10 min. when copper is precipitated as cupric sulphide and the precipitate is filtered. The filtrate is boiled for 20 minutes to remove hydrogen sulphide gas. The boiling is continued to reduce the volume of the filtrate. To the filtrate 3 ml of 8-hydroxy quinoline reagent is added drop by drop with constant stirring. Add drop by drop concentrated ammonia solution till the pH of the solution becomes 9.3. The precipitate is filtered through sintered crucible and washed with hot water and dried. A duplicate experiment is carried out.

(OR)

Complexometric method

Zinc can be estimated by following the procedure for estimation of magnesium in dolomite.

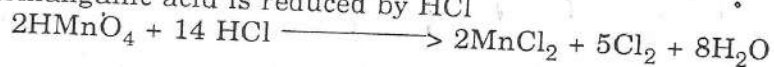
3. ESTIMATION OF CHROMIUM AND NICKEL IN STAINLESS STEEL

Principle

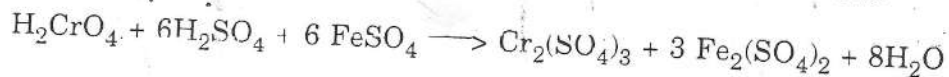
Nickel is estimated gravimetrically by precipitating as Ni-DMG using an alcoholic DMG as the precipitant. The chromium is oxidised to chromate by persulphate solution in the presence of AgNO_3 (catalyst) the reaction may be represented as follows:



The permanganic acid is reduced by HCl



H_2CrO_4 reacts with H_2SO_4 and FeSO_4 in the solution as follows



To the solution excess of known amount of FAS is added and then excess of FAS is back titrated with standard KMnO_4 .

Procedure

Preparation of Alloy Solution

About 1 g of stainless steel is weighed and taken in a 400 ml beaker. Added 30 ml of H_2SO_4 - H_3PO_4 mixture (prepared by adding slowly 100 ml of 1:1 H_2SO_4 to 300 ml of water cooling mixing with 40 ml of H_3PO_4) Heat it until the effervescence ceases then added continuously 4.5 ml of Con. HNO_3 and boiled until the solution is free from the oxides of Nitrogen. Dilute the solution into 200 ml with distilled water and added 5 ml of AgNO_3 solution (5g of AgNO_3 per 1000 cc) and 15-20 ml of freshly prepared 10% solution of Ammonium persulphate solution. Boiled the solution for 10 min. Added 5 ml of dil. HCl (1:3) to the hot solution boil for 10 min after the permanganate color had disappeared cool the solution and made upto the mark into a 250 ml standard flask using distilled water.

Estimation of chromium

From the steel solution 10 ml is pipetted out into a clean conical flask added 20 ml of 0.05 N. FAS and it is back titrated against standard KMnO_4 until a pink color is obtained. The titration is repeated for concordance. KMnO_4 is standardised by FAS.

Estimation of Nickel

Amount 10 ml of the solution is pipetted out and added about 4 ml of 1% alcoholic DMG followed by Ag.NMH_3 slowly and constant stirring till the precipitation is complete. This is digested for 30 min and tested for complete precipitation. The precipitate is filtered through a previously weighted sintered crucible and the precipitate is washed with ag. NH_3 and dried in oven at 100°C . A duplicate is also conducted.

C. ANALYSIS OF INORGANIC COMPLEX COMPOUNDS

1. PREPARATION OF CIS AND TRANS DIOXALATO DIAQUOCHROMATE AND ANALYSIS OF EACH OF THESE FOR CHROMIUM

(A) The trans isomer, $K [Cr(C_2O_4)_2(H_2O)_2]$

Chemicals required : Oxalic acid and Potassium dichromate

Procedure

Dissolve oxalic acid dihydrate (12 g) in minimum amount of boiling water. It is advisable to use a beaker of not less than 300 ml capacity, since the ensuing reaction is rather vigorous. Add, in small portions, a solution of potassium dichromate (4g) dissolved in the minimum quantity of hot water, covering the beaker while violent reaction proceeds. Evaporate the solution to about one half of its original bulk and then allow spontaneous evaporation at room temperature to proceed until the solution is reduced to about one third of its original bulk. Filter off the crystals, wash with cold water, and alcohol. Record the yield, and express this as a percentage based on chromium. A high yield cannot be expected since only part of the product is isolated.

Note that in solution there is an equilibrium between the cis - and trans-isomers, but the low solubility of the trans isomer result in its initial deposition. Excessive spontaneous evaporation should be avoided otherwise the product may be contaminated with the cis isomer.

B. The cis Isomer, $K [Cr (C_2O_4)_2 (H_2O)_2]$

Chemicals required : as in (a) + ethanol

Procedure

Prepare an intimate mixture of finely ground potassium dichromate (4 g) and oxalic acid dihydrate (12 g) and heat the powder in 6 inch diameter evaporating dish. Place one drop of water in a small depression in the mixture and cover the dish with a watch glass. After a short induction period the reaction commences and soon becomes vigorous with the evolution of steam and CO_2 . A solution of the product is avoided, and hence an equilibrium mixture of cis and trans isomers is not formed.

The product of this reaction is a purple viscous liquid over which is poured 20 ml of ethanol and the mixture stirred until the product of the reaction solidifies. If solidification is slow, decant the liquid and repeat the process with a second portion of alcohol until the product is entirely crystalline, Filter, dry at the pump, and record the yield.

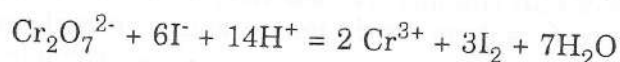
ANALYSIS

Chromium estimation

Almost any standard analytical procedure may be adopted; the following is a typical example. A known weight of the complex is dissolved in dilute sulphuric acid and oxidised by boiling with potassium bromate for 10 minutes. The excess potassium bromate is destroyed by adding ammonium sulphate and boiling until nearly all the excess of bromine has been volatilized. Add 5 ml of 2 M hydrochloric acid and boil until free halogen is no longer evolved. The resulting dichromate solution may now be determined by a standard iodimetric procedure.

Procedure

Place 100ml of cold, recently boiled distilled water in a 500 ml of conical, preferably glass stoppered, flask, add 3 g. of iodate free potassium iodide and 2 g. of pure sodium carbonate, and shake until the salt dissolves. Add 6 ml of concentrated HCl slowly whilst gently rotating the flask in order to mix the liquids; run in 25 ml of resulting potassium dichromate solution. Stopper the flask in order to mix the liquids; run in 25 ml of resulting potassium dichromate solution. Stopper the flask and allow to stand for minutes. Dilute the solution to 300 ml and titrate the liberated iodine against standardised sodium thiosulphate solution contained in the burette. When most of the iodine has reacted as indicated by the solution acquiring a yellowish green colour, add 2 drops of starch solution and rinse down the sides of the flask. Colour changes to shades of blue. Continue the addition of thiosulphate until the colour changes from greenish blue to light green. Carry out the blank titration after substituting for potassium dichromate with distilled water.



2. PREPARATION OF POTASSIUM TRIS OXALATOFERRATE(II). AND ANALYSIS FOR OXALATE AND IRON

Preparation

Dissolve 3.8 gm of ferrous ammonium sulphate in 15 ml of water. Add 1 ml of ammonium sulphate followed by a solution of oxalic acid containing 2 gm in 10 ml of water. Stir the contents over a stirrer for about 5 minutes. Decant the clear liquid and wash the precipitate with water. Transfer the above precipitate into a warm solution of potassium oxalate containing 2.5 gm in 30 ml of water. Add slowly from a burette 15 ml of 20% H_2O_2 , stir the liquid continuously during the addition keeping the temperature near to 40°C . Heat the mixture to boiling and dissolve the precipitate by adding 10 ml of 10% oxalic acid (in one lot) and then if necessary in drops till clear solution is obtained. Filter the hot solution, collect it in a beaker covered with black paper and add 20 ml of acetone to the filtrate and keep it aside in dark for crystallisation. Filter the crystals using G3 sintered crucible and wash it with 1:1 acetone after mixture. Followed by acetone and dry it in air. Note the yield.

ANALYSIS

Weigh accurately around 1 gm of the complex and transfer it into 100 ml standard flask. Add 10 ml of 4 N H_2SO_4 . Dissolve and make upto the mark and mix well.

Analysis of Oxalate

Pipette out 10 ml of made up solution and add 5 ml of 4 N H_2SO_4 and heat to boiling. (80°C) Titrate the hot solution with 0.05 N KMnO_4 till a pale pink colour is formed.

$$\% \text{ of Oxalate} = \frac{V_1 \times N_1}{10} \times \frac{44.01 \times 100}{10 \times \text{wt}}$$

V_1 = volume of KMnO_4
 N_1 = Normality of KMnO_4
 Wt = wt. of sample in 100 ml

Analysis of Iron

To the titrated solution (after oxalate estimation), add 5 ml of conc. HCl heated to boiling and add SnCl_2 (15% in 1:1 HCl) till the appearance of yellow colour. Add one drop in excess and cool. Add 5 ml of 5% HgCl_2 in one lot. Silky white precipitate should be formed (Grey colour. Repeat the experiment) Add 2 ml of phosphoric acid and 2 drops of diphenylamine indicator and titrate against standard $\text{K}_2\text{Cr}_2\text{O}_7$ (0.05N) till a bluish violet colour is formed.

$$\text{Fe}^{3+} \% = \frac{V_1 \times N_1}{10} \times \frac{55.85 \times 100}{10 \times \text{wt}}$$

V_1 = volume of $\text{K}_2\text{Cr}_2\text{O}_7$
 N_1 = Normality of $\text{K}_2\text{Cr}_2\text{O}_7$
 Wt = wt. of sample in 100 ml

D. QUANTITATIVE ANALYSIS

1. MIXTURE OF IRON AND MAGNESIUM

Principle

In this process, iron is first converted to ferric state by hydrogen peroxide, using concentrated ammonia it is precipitated as ferric hydroxide and subsequently it is estimated in the form of ferric oxide after ignition. Magnesium is estimated using EDTA titration in the presence of Eriochrome black T as indicator.

Procedure

Weigh out accurately about 0.5 g of the mixture in a beaker and add slowly 10 ml of concentrated nitric acid. When the reaction is almost over, warm the mixture on a hot plate until the mixture has completely dissolved. Add 10 ml of water, and allow the solution to digest for 10-15 minutes.

Add 1 to 2 ml of hydrogen peroxide to the solution to oxidise the iron to Ferric state. Add a large excess of concentrated ammonia solution, and heat to boiling. Filter off dissolve precipitate in the minimum volume of hot 1:1 hydrochloric acid, and receive the acid solution in a small beaker. Pour in enough 1:2 - ammonia solution to reprecipitate the ferric hydroxide, heat to boiling, filter and wash the precipitate. Add the filtrate and washings to the main filtrate. Ignite the precipitate, and weight the ferric oxide.

Dilute the filtrate to 250 ml in a volumetric flask. Shake well to mix thoroughly. Take a aliquot, adjust the pH with a monoethanol amine hydrochloride buffer and titrate with standard 0.02 M - EDTA but using Eriochrome Black T as indicator. Calculate the percentage of Mg.

1 ml 0.02 M - EDTA = 0.4864 mg . Mg.

2: MIXTURE OF IRON AND NICKEL

Principle

The iron in the mixture is estimated as ferric oxide. In this process, iron is first converted to ferric state by hydrogen peroxide, using concentrated ammonia it is precipitated as ferric hydroxide and subsequently it is estimated in the form of ferric oxide after ignition.

Nickel is estimated as Nickel DMG complex.

Procedure

Weigh out accurately about 0.5 g of the mixture in a beaker and add slowly 10 ml of concentrated nitric acid. When the reaction is almost over, warm the mixture on a hot plate until the mixture has completely dissolved. Add 10 ml of water, and allow the solution to digest for 10 - 15 minutes.

Add hydrochloric acid to the filtrate till it becomes neutral and add 5 ml excess. Add the ammonia solution slowly until the solution is slightly ammoniacal. For each 0.1 g of Nickel that is expected to be present, add to the hot solution 0.5 g of dimethylglyoxime dissolved in rectified spirit, and make certain that the solution is slightly ammoniacal. Allow the beaker to stand on the steam-bath for 15 - 20 minutes, and test the solution for complete precipitation after the red precipitate has settled out. Allow the precipitate to stand for 1 hour, cooling at the same time. Filter the cold solution through a Gooch, sintered glass or porcelain filtering crucible, previously heated to 110 - 120°C and weighed after cooling in a desiccator. Wash the precipitate with cold water until free from chloride, and dry it at 110 - 120°C for 45 - 50 minutes. Allow to cool in a desiccator and weigh. Repeat the drying until constant weight is attained. Weigh as $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$, which contains 20.32 per cent of Ni.

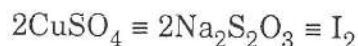
3. MIXTURES OF COPPER AND NICKEL

Principle

Copper is estimated iodimetrically in the presence of Nickel by titration with liberated iodine against thio using starch as Indicator.



from this,



Nickel is estimated after removing Cu by passing H_2S in slightly acidic medium and removed by filtration to the filtrate solution alcoholic DMG and aq. NH_3 are added and Nickel present is precipitated as Nickel DMG.

Procedure

Standardisation of Thio

About 2.5 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is accurately weighed and it is made up to 100 ml by using distilled water. In a 100 ml standard flask 20 ml of the solution is settled out into a clean conical flask to this add aq. NH_3 solution till $\text{Cu}(\text{OH})_2$ is precipitated till the solution becomes dark blue solution and to this acetic acid is added in drops till the solution is acidic then added 10 ml of 10% KI and titrated against this using

starch as indicator. The end point is disappearance of brown colour and the appearance, of white color. The titration is repeated for concordant values.

Preparation of Alloy Solution

About 1.5g of Cu-Ni alloy is weighed and dissolved in con. HNO_3 it is diluted with water and concentrated by evaporation, cooled and made upto 250 ml in a standard flask using distilled water.

Estimation of Copper

From the alloy solution 20 ml is pipetted out into a clean conical flask. To this added ag. NH_3 is drops till there is CH_3COOH smell. Then added 10 ml of 10% KI solution and titrated against this solution using starch as indicator. The end point is disappearance of dark brown color to appearance of white color. The titration is repeated for concordant value.

Estimation of Nickel

20 ml is pipetted out into conical flask and acidified with 10 ml of con.HCl to the above solution H_2S is passed. Copper present in the solution is precipitated as CuS and it is filtered off. The filtrate is tested for copper with H_2S . If there is any precipitate it is removed by filtration. The filtrate is boiled to remove H_2S and added 5 ml of alcoholic DMG solution slight excess of aq. NH_3 solution in drops with constant stirring the precipitate is kept in the steam bath for half an hour and then filtered through a sintered crucible. The precipitated is washed with ag. NH_3 and dried at 110°C and weighted. A duplicate experiment is performed.

(2)

4. MIXTURE OF COPPER AND ZINC

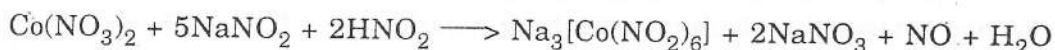
(See estimation of Brass)

PART II

PREPARATION OF THE COMPLEXES

1. SODIUM HEXANITROCOBALTATE(III)

Dissolve 30 gm of sodium nitrite in 30 ml of hot water. Cool the solution to 50°C and dissolve in it by stirring 10 gm of Cobalt nitrate crystals. Add drop by drop from burette 10 ml of 50% acetic acid to the continuously stirred solution:



Transfer the brown liquid to a filter bottle, which is then closed with a cork carrying an inlet tube reaching to the base of the bottle. With the aid of the filter-pump draw a current of air through the liquid for about 30 minutes to remove excess nitrous acid. If any yellow crystals are then seen in the liquid (originating from the potassium salt contaminating the sodium nitrate used) these filtered off by suction; the clean brown filtrate is placed in a beaker surrounded by an ice-bath, and mechanically stirred while 50 ml of ethanol are added drop by drop from tap funnel. The bright orange precipitate is filtered by suction, washed several times with ethanol, and then dried in warm air. Yield, 13-14 g.

2. TRIS (ETHYLENEDIAMINE) COBALT (III) CHLORIDE

Chemicals required

Ethylene diamine	-	3.25 ml
CoCl_2	-	6 g
Conc. HCl	-	1.5 ml
Alcohol	-	10 ml

H_2O_2

Procedure

The ethylenediamine solution is partially neutralised with Conc. HCl and the resulting mixture is poured slowly into a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in small amounts of water. The solution is oxidised using small amounts of H_2O_2 slowly. The crystals of tris (ethylenediamine) Cobalt (III) chloride are filtered, washed with alcohol and dried.

3. CHLOROPENTAMMINE COBALT (III) CHLORIDE

Chemicals required

Aq. NH_3	-	6 ml
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	-	2 g
NH_4Cl	-	1 g
Conc. HCl	-	6 ml
Alcohol	-	20 ml

Procedure

About 1 g of NH_4Cl is dissolved in 6 ml of Con. NH_3 . The solution is continuously agitated to which 2 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is added in small portion, each portion being dissolved before next is added. A yellow pink precipitate of hexamine Cobalt (II) Chloride forms with the evolution of heat. To warm, slurry 2 ml of 30% H_2O_2 is added with good stirring. This results in vigorous reaction with effervescence. When effervescence ceases a deep red solution of aquo pentammine salt has formed. To this, 6 ml of Conc. HCl is added slowly. During neutralisation, the temperature of the reaction mixture rises and purple product ppt. bearing a pale yellow green liquid. The mixture is heated for about 15 minutes on a steam bath, cooled to room temperature and filtered. The precipitated product is washed with several portion of ice cold water. An alcohol wash followed by an acetone wash facilitate drying which is accomplished by heating the product at $100-119^\circ\text{C}$ for 1-2 hours.

4. BIS(ACETYLACETONATO) COPPER (II)

Chemicals required

Cupric sulphate, Acetylacetone, Sodium hydroxide and glacial acetic acid.

Procedure

Weigh about 5 g of cupric sulphate in 250 ml beaker and dissolve it in minimum amount of water 4.3 ml of acetylacetone and 1.6 g of sodium hydroxide in aqueous solution is added. The precipitate thus obtained is dried over H_2SO_4 in vacuum and recrystallised twice from glacial acetic acid as steely blue needles.

5. HEXAMMINECOBALT (III) CHLORIDE

In boiling solution of 12 gm of ammonium chloride in 25 ml of water dissolve 18 gm of Cobaltous chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ place 1 gm of decolourising charcoal in a dry flask, introduce the hot solution and then cool the whole in running water. Wash out the vessel in which the solution is first made with 40 ml of concentrated ammonia ($d = 0.880$), and then add the ammoniacal liquid to the flask. Cool the whole preparation in an ice - bath to 10°C (or lower). Add slowly, in portions, while briskly shaking the flask and its contents, 35 ml of H_2O_2 . All the oxidizing agent having been added, heat the mixture gradually to 60°C , and then maintain the temperature in the range $50-60^\circ\text{C}$, with frequent mixing by shaking, until a pinkish tint in the liquid is removed. (20 min). Crystals begin to separate at the close of the heating, and are deposited in quantity on cooling in an ice - bath.

$$2\text{CoCl}_2 + 2\text{NH}_4\text{Cl} + 10\text{NH}_3 + \text{H}_2\text{O}_2 \longrightarrow 2\text{Co}(\text{NH}_3)_6\text{Cl}_3 + 2\text{H}_2\text{O}$$
after which clear solution is poured in conc. HCl . After heating for few minutes in a steam bath, the complex can be isolated.

what is the colour of the complex?

6. HEXAMMINENICKEL (II) CHLORIDE

Dissolve 6 g of Nickel chloride in 10 ml of warm water (and filter the solution if it is not quite clear). Mix well 10-12 ml (7-8 mol.) of concentrated aqueous ammonia ($d = 0.880$) with the solution, until all initial green precipitate Nickel hydroxide has redissolved, and the liquid, deep blue in colour, contains a copious crystalline deposit of the violet coloured hexammineNickel(II) chloride.

7. DIISOTHIOCYANATO DIPYRIDINE MANGANESE(II)

Chemicals required

MnSO₄ 5H₂O - 1.7 g
Pyridine - 3.5 ml
Ammonium thio cyanate - 1.52 g

Procedure

1.7 g of Manganese sulphate pentahydrate is dissolved in 50 ml of distilled water containing 3.5 ml pyridine. This solution is added slowly with stirring a solution of 1.52 g of Ammonium thiocyanate in 10 ml of distilled water and the resulting mixture is allowed to stand in an ice bath until precipitation appears. Completed (continuously for an hour) the precipitate is filtered through Buckner funnel and is washed with three 10 ml portions of an ethanol - pyridine (9:1) solution. The product is air dried not more than 10 minute. The product is white in colour.

SPECTRAL ANALYSIS

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance absorption

Nuclear magnetic resonance (NMR) spectroscopy is one of the most advanced methods of structural investigation in coordination chemistry. Nuclear magnetic resonance arises from the phenomenon that, according to quantum mechanics, the magnetic moment of a nucleus (μ) assumes quantised orientation in an external magnetic field H_k , where the preferential orientation is the one aligned with the field. The possible values of the interaction energy (E_m) between the nuclear magnetic moment and the external magnetic field are :

$$E_m = h\gamma H_k m \text{ where } m = I, I-1, \dots -I \dots \quad (1)$$

where γ is the gyromagnetic ratio for the nucleus, h is the plancks constant divided by 2π , m is the magnetic quantum number, having $2I+1$ possible values and I is the nuclear spin quantum number. The contribution to the energy of the nucleus arising from the interaction with the uniform magnetic field H_k can be characterised by $2I+1$ energy levels; the gap between the levels increases linearly with the strength of the magnetic field. By absorption of electromagnetic radiation of suitable energy and polarity transitions corresponding to the selection rule $\Delta m = \pm 1$ can be induced between these energy levels. The angular frequency of the electromagnetic radiation inducing the transition is

$$\omega_r = rH_k \quad (2)$$

transition between adjacent energy levels will be induced only by radiation of angular frequency which satisfies (2). Consequently, the transition has a resonance character.

The nucleus under investigation interacts with its environment. Therefore the frequency dependence of energy absorption will not appear as an extremely narrow line corresponding to equation (2) but, similarly to other spectral lines, will have a definite shape and width and splitting on various interactions.

The difference in resonance field strength for nuclei in two different environments is called the chemical shift, and is generally expressed in parts per million relative to some standard nucleus

$$\delta = \frac{H_{\text{sample}} - H_{\text{reference}}}{H_{\text{reference}}} \times 10^6$$

In the case of proton magnetic resonance of organic compounds, Tetramethylsilane (TMS) is commonly used as a reference compound.

An NMR spectrum is a plot of chemical shift vs percentage intensity of absorption. An NMR can be characterised by the following parameters of the absorption peaks.

1. position
2. width
3. shape
4. integral intensity

The measurements and theoretical analysis of these parameters provide information on the immediate environment of the nucleus.

Results obtainable by the NMR technique

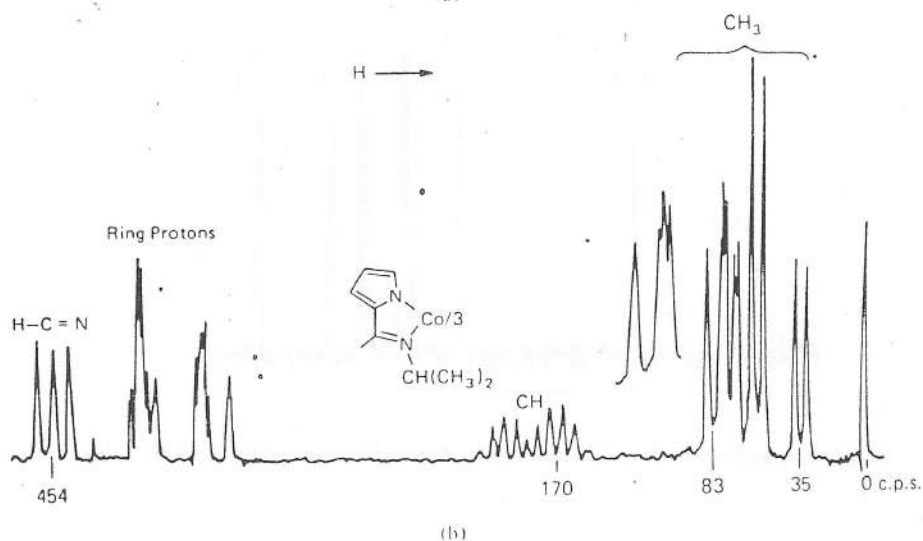
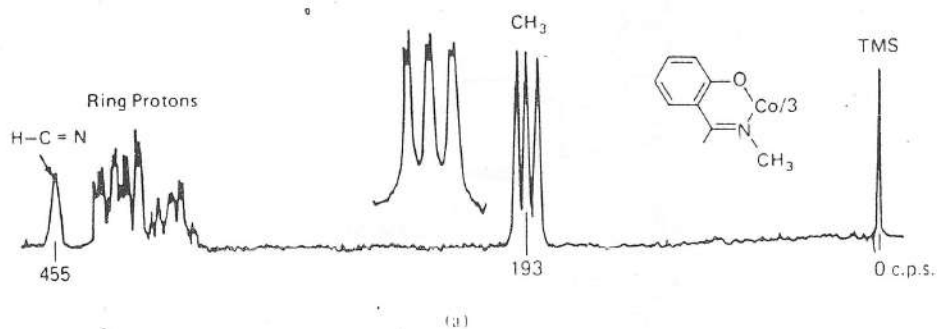
NMR spectra may yield the following information about a molecule :

1. The position of the resonance frequency (ie. chemical shift) provides information on the environment of the magnetic nuclei in the molecule. At the same time, it allows the identification of the magnetic nuclei.
2. The relative ratio of equivalent nuclei in the molecule can be determined from the intensity distribution of the corresponding resonance lines.
3. The fine structure of the spectrum of a nucleus or an equivalent nuclear group provides information on the spin of the other nuclei present in its vicinity, and on the number of equivalent, interacting nuclei in the nuclear group.
4. Analysis of the fine structure permits, on the basis of the differences in the values of the spin-spin coupling constant, determination of the spatial arrangement of the nuclei.
5. The investigation of the σ -shielding tensor also yields information on the spatial arrangement of the nuclei studied. This means that the magnetic shielding of the atomic nuclei depends not only on their nature and bonding, but also on the spatial arrangement of the neighbouring atom.

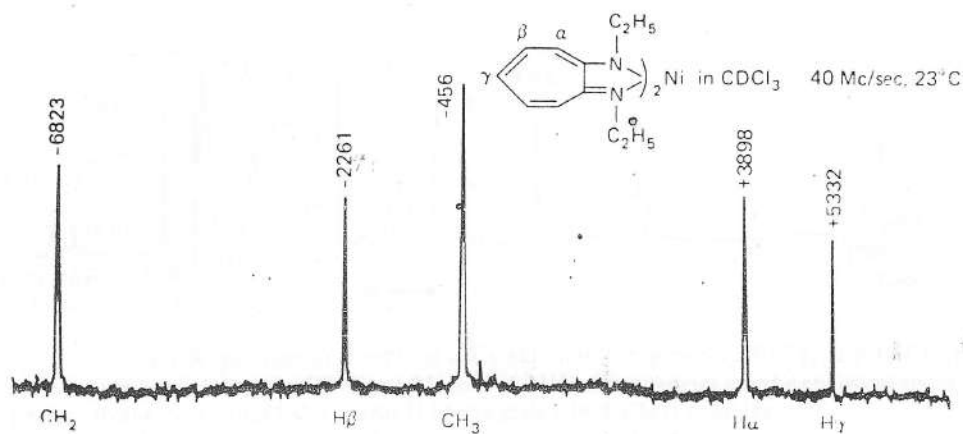
Nuclear spin, magnetic moment and resonance frequency values of elements

Nucleus	Natural-isotopic abundance	Nuclear spin	Nuclear magnetic moment	Frequency
^1H	99.99	$1/2$	2.792	42.59
^2H	0.01	1	0.857	6.53
^{11}B	81.00	$3/2$	2.688	13.66
^{12}C	98.9	0	-	-
^{13}C	1.1	$1/2$	0.702	10.70
^{14}N	99.6	1	0.404	3.07
^{15}N	0.4	$1/2$	-0.283	4.21
^{16}O	99.7	0	-	-
^{17}O	0.04	$5/2$	-1.892	5.77
^{18}O	0.2	0	-	-
^{19}F	100	$1/2$	2.6289	40.09
^{31}P	100	$1/2$	1.1316	17.25°
^{35}Cl	75.39	$3/2$	0.8218	4.17
^{37}Cl	24.61	$3/2$	0.684	3.47
^{127}I	100	$5/2$	2.808	8.56

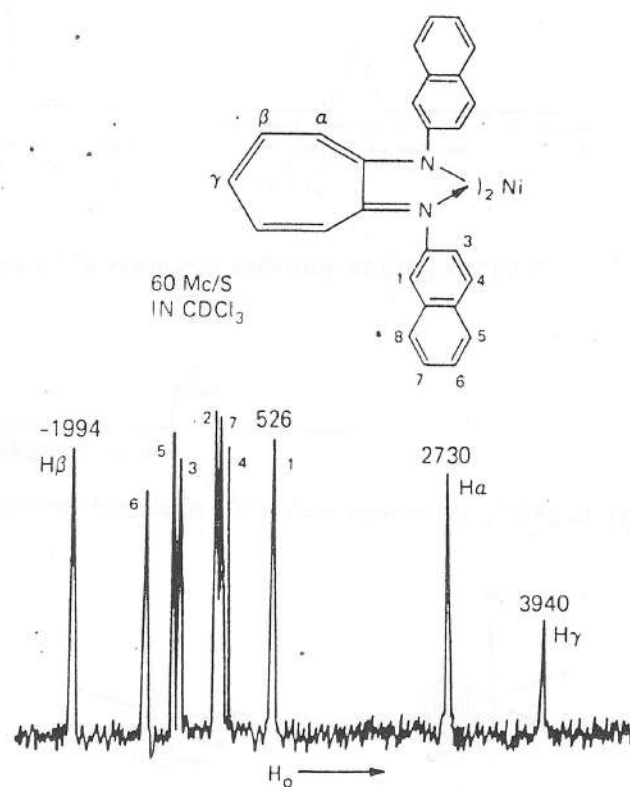
Interpret the following NMR spectra



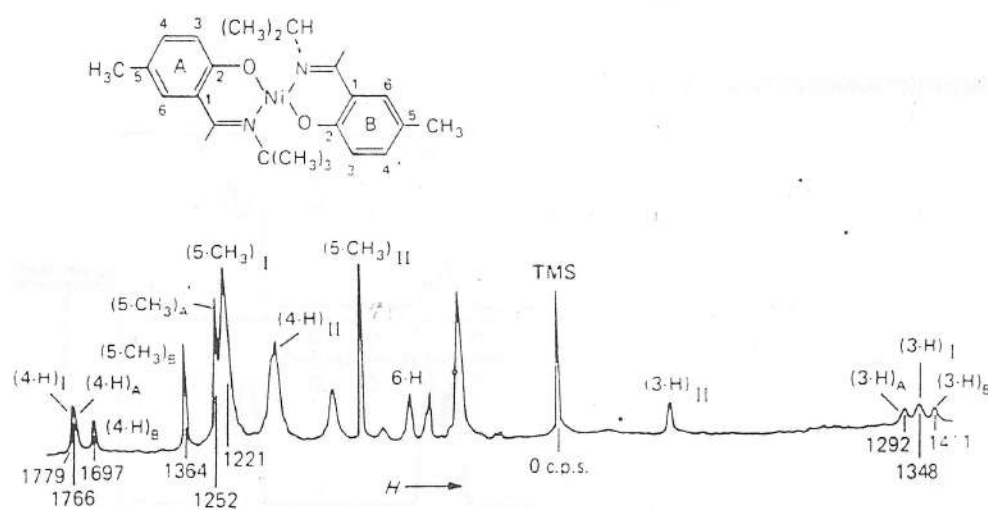
Proton resonance spectrum of (a) tris-*N*-methylsalicylaldimino Co(III) and (b) tris-*N*-isopropylpyrrole-2-aldimino Co(III) in CDCl₃. The insert in (a) shows the N-CH₃ signals on an expanded scale. The insert in (b) shows a portion of the isopropyl methyl signals on an expanded scale.



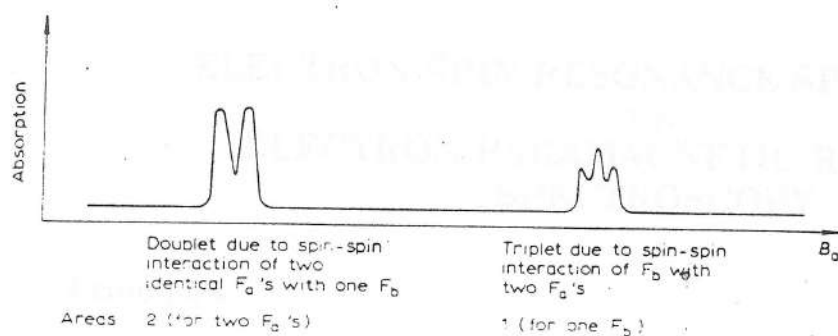
PMR spectrum of bis(*N,N'*-diethylaminotroponeimino)Ni(II).



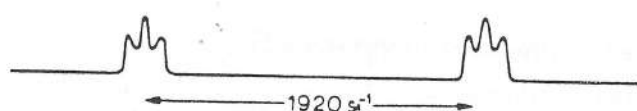
PMR spectrum of bis(*N,N'*-di- β -naphthylaminotroponeimino)Ni(II).



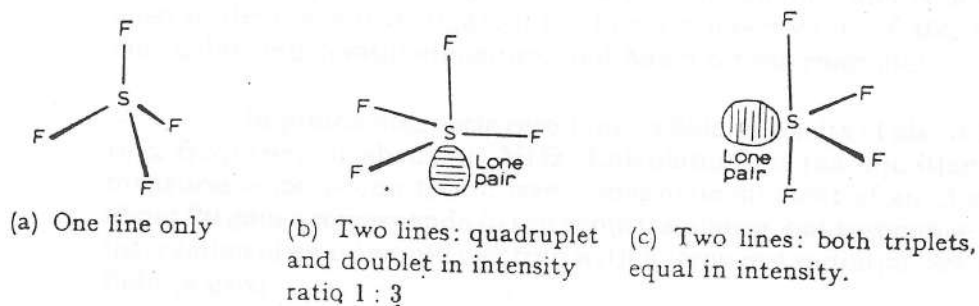
PMR spectrum of the mixed salicylaldimino complex *i*-Bu(5-CH₃)-*i*-Pr(5-CH₃) and its pure components in CDCl₃ at 25° and 60 MHz. Frequencies are the chemical shifts. I refers to the pure *i*-Bu(5-CH₃) and II to the pure *i*-Pr(5-CH₃) complex.



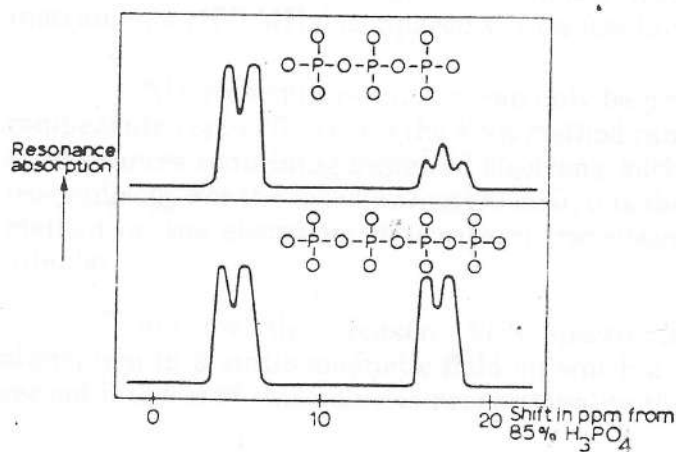
High-resolution ^{19}F resonance spectrum of ClF_3 at 220 K.



Pair of resonance triplets in ^{19}F n.m.r. spectrum of SF_4 at 180 K.



Types of n.m.r. spectra consistent with three hypothetical structures.



^{31}P n.m.r. spectra of tripolyphosphate and tetrapolyphosphate ions.

ELECTRON SPIN RESONANCE SPECTROSCOPY (OR) ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

Principles

The fundamental principles of Electron spin Resonance (EPR) are essentially the same as those of NMR. Practical differences arise from the fact that the magnetic moment of an electron is substantially larger than that of a proton.

The energy of resonance absorption is

$$\Delta E = h\nu = g\beta H,$$

where, ν denotes the frequency of radiation used, h is the planck's constant, " g " is the spectroscopic splitting factor, β is the Bohr magneton, and H is the magnetic field. In most of the cases investigated, the factor g has a value of about 2, depending on the molecular and crystal structure, and has a tensor character.

In proton magnetic resonance a field intensity of about 10,000 G corresponds to a frequency of about 40 MHz. Calculation on the equation shows that in ESR measurements, owing to the larger magnetic moment of an electron, an intensity of about 20 gauss corresponds to the same frequency, but resonance conditions producing interaction of an unpaired electron with microwave radiation are satisfied if a stronger field is used.

Therefore the EPR or ESR instruments used in practice operate in the region of 9,000 mega hertz (3 cm wavelength) or 36,000 MHz (8 mm wavelength). The corresponding field intensities are about 3,300 and 13,000 gauss respectively. For technical convenience, a higher modulation frequency is generally used with ESR instruments (100 MHz) compared with a few hundred cycles (Hz) in NMR.

Electron spin resonance can only be produced by electrons possessing non-compensated spin. Therefore the ESR method can only be applied to the investigation of substances containing unpaired electrons, such as transition metal complexes and free radicals. For the coordination chemist, it is the information obtainable by the ESR method on the electronic structure of transition metal ions which is of particular interest.

For technical reason, ESR spectrometers give the differential of the absorption in a static magnetic field on which a varying field is superimposed. The second integral of this value is proportional to the concentration.

The ESR spectrum can be represented by plotting intensity against the strength of the applied field but ESR spectra are commonly presented as derivative

curves, i.e. the first derivative (the slope) of the magnetic field. Much greater sensitivity can be achieved by this detection method if the line shape is broad.

One important characteristic of an ESR spectrum is the field strength at which resonance occurs, or what is more fundamental, the g value. In the case of split signals, the g value corresponds to the centre of gravity of the signal. Every paramagnetic substance is characterised by a unique g value, which is formally analogous to the chemical shift value of NMR spectrometry.

SCOPE OF ESR SPECTROSCOPY

The area under the ESR absorption curve is proportional to the number of unpaired electron in the sample. The sensitivity of the method permits determination even if this number is as low as 10^{11} . This high sensitivity renders the method suitable for the investigation of transition metal complexes of low solubility.

Hyperfine splitting

Electronic spin can couple with nuclear spin and therefore ESR signals will generally be split into hyperfine multiplets whenever the unpaired electrons are in the vicinity of magnetic nuclei.

Each ESR signal of an electronic system that interacts with a group of " n " equivalent nuclei of spin I is split into $(2nI+1)$ lines.

Interpretation of ESR spectra

ESR spectra of Mn^{2+}

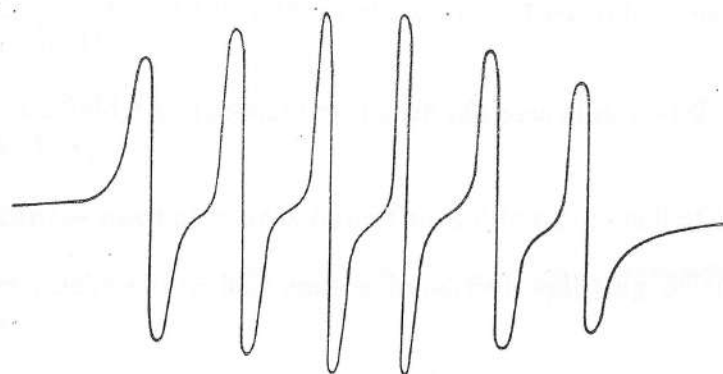
1. What is zero field splitting?

A species containing one unpaired electron can have its spin degeneracy removed only by application of a magnetic field. The same is true for a species containing more than one unpaired electron, as long as there is no appreciable magnetic interaction between the unpaired electrons. For example, for a triplet species ($S = 1$ and $M_s = +1, 0, -1$) in which there is no magnetic interaction. In the absence of a magnetic field the three spin states are degenerate and are split upon application of a field. In this case the two allowed transitions occur at the same field strength and only one ESR resonance is observed. However, if there is appreciable magnetic interaction between the two electrons, the different M_s states have different energies even in the absence of a magnetic field. This is called as zero field splitting.

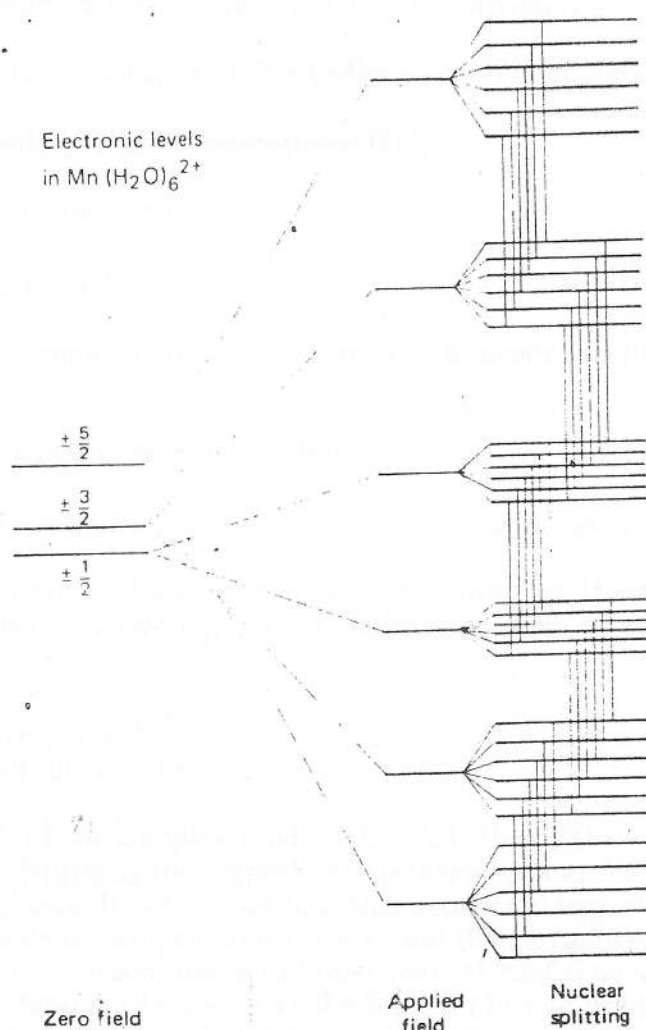
2. How many states are possible for Mn^{2+} ion $(Mn(H_2O)_6)^{2+}$ under zero field splitting.

There are three states are possible under zero field splitting.

They are $+1/2$, $+3/2$ and $5/2$



The esr spectrum of aqueous Mn^{2+} .



Electronic levels in $\text{Mn}(\text{H}_2\text{O})_6^{2+}$.

3. How the degeneracy of these three states are lifted under the influence of a magnetic field?

In a magnetic field, the degeneracy of each of these states $+1/2$, $+3/2$ and $5/2$ is lifted, yielding six states.

4. How manganese nucleus causes hyperfine splitting of each of these states?

Manganese nucleus ($I = 5/2$) causes hyperfine splitting of each of these states into six states.

5. How many primary splitting occurs in $(\text{Mn}(\text{H}_2\text{O})_6)^{2+}$ ESR spectrum?

There are five transitions possible for six states.

6. How many secondary splitting is possible for $\text{Mn}(\text{H}_2\text{O})_6^{2+}$?

The ESR spectrum consists of five peaks each split into six components.

ESR Spectra of bis(salicylaldimine)copper(II)

1. What is the I value of ^{63}Cu ?

I value of $^{63}\text{Cu} = 3/2$

2. How many resonances are possible by the hyperfine splitting of copper nucleus?

There are four main resonances possible.

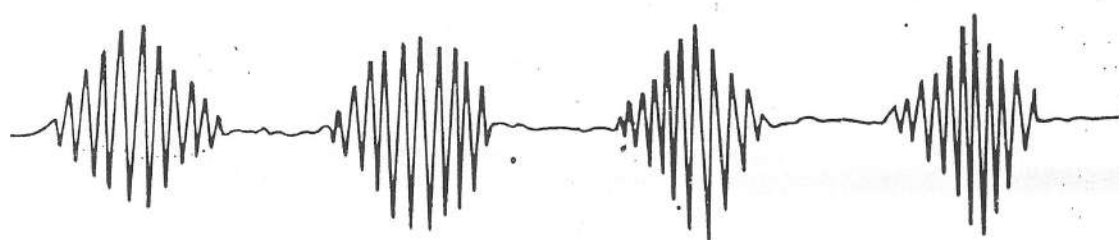
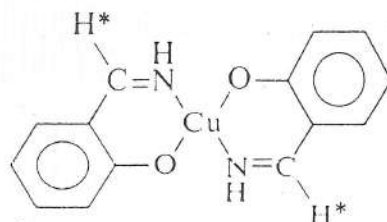
$$(2 \times 1 \times 3/2 + 1) = 4$$

3. What is the nature of hyperfine splitting caused by the two equivalent nitrogen atoms and two equivalent hydrogen atoms attached to carbon atom?

I value for nitrogen = 1

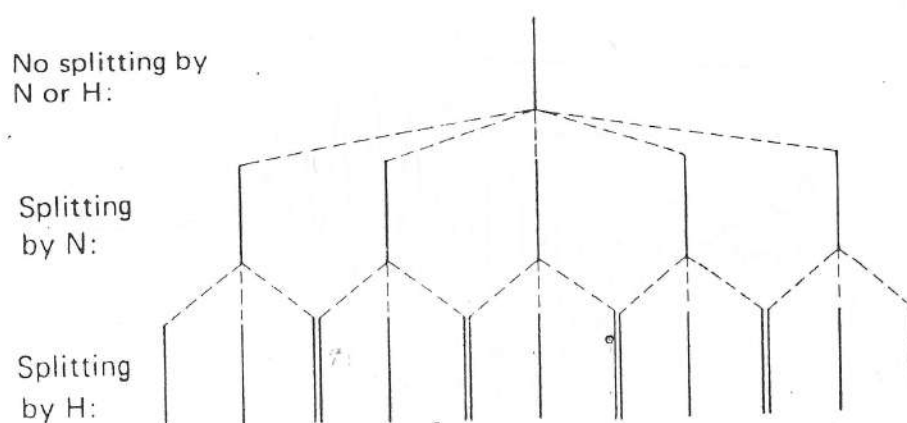
I value for hydrogen = $1/2$

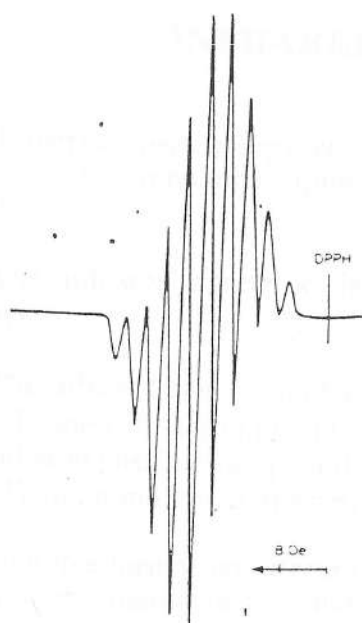
The spectrum of the complex made with ^{63}Cu ($I = 3/2$) consist of 4 main resonances (hyperfine splitting by the copper nucleus) each resonances being split into what appears to be 11 peaks. It is believed that this secondary hyperfine splitting is caused by the two equivalent nitrogen atoms ($I = 1$) and the two equivalent hydrogen atoms ($I = 1/2$) attached to carbon atoms (marked with *), and thus we expect each multiplet to consist of a total of $(2 \times 2 \times 1 + 1)(2 \times 2 \times 1/2 + 1) = 15$ lines. The fact that only 11 lines are observed is explained by assuming that four of the proton hyperfine lines coincide with four of the nitrogen hyperfine lines as shown below.



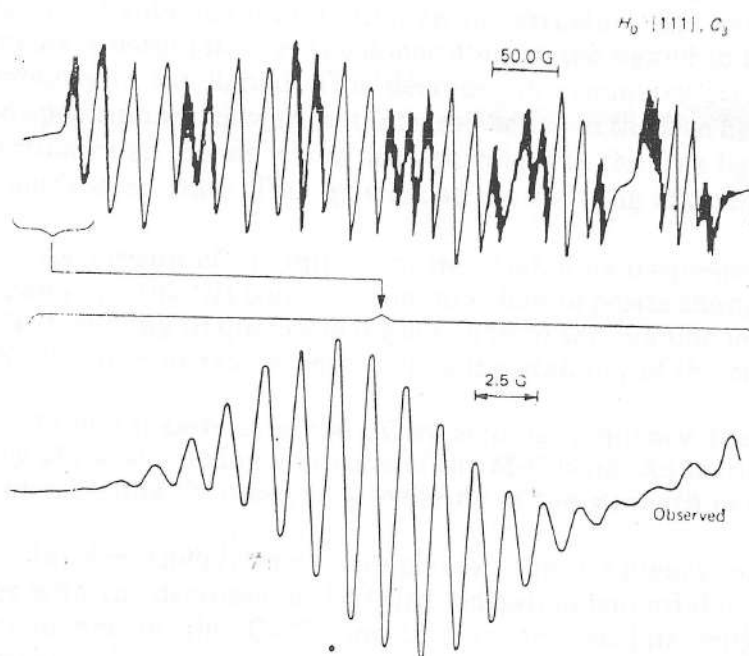
The esr spectrum of bis(salicylaldehyde)copper(II).

hyperfine lines coincide with four of the nitrogen hyperfine lines, as shown below.





ESR spectrum of an acetonitrile solution of $\text{Cr}(\text{Et}_2\text{dtc})_3$



ESR spectrum of MnCl_4^{2-} in K_4dCl_6 with the magnetic field parallel to the threefold axis of the octahedron (top). The chlorine hyperfine splitting on one of the manganese transitions is enlarged (bottom).

INFRARED SPECTROSCOPY

Infrared spectroscopy is used by chemists for three different purposes, identification of compounds, quantitative analysis of mixtures and structure determination.

The infrared spectrum is a plot of percentage transmittance against wavenumber.

The infrared spectrum of a compound may be used as a "fingerprint" of the compound. To identify a compound its spectrum is compared with the spectra of a limited number of possible compounds with suggested properties and the source of the compound. When a matching spectrum is found, identification is complete.

Complex formation affects the vibration of the ligand. Co-ordination of the donor atom of the ligand to the central atom changes the symmetry of the ligand. Complexation alters the electron density on the individual atoms of the ligand, and therefore bond orders, etc. in the ligand are changed. The formation of the chelate rings offers new possibilities of these factors cause certain changes in the infrared spectrum of the ligand. Shifts in the IR absorption of the ligand on complex formation may also yield valuable information on the structure and bonding characteristics of the complex. Coordination of the donor atom of the ligand to the central atom lowers the symmetry of the ligand. This decrease in symmetry gives rise to bands in the infrared spectrum which were not infrared active in the free ligand in accordance with the selection rules. Bonds which are equivalent in the free ligand are not equivalent in the coordinated state. This may cause the splitting of certain bands.

As a result of co-ordination, the stretching frequencies of the $\text{C}\equiv\text{N}$ bond in cyano ligand and the NH bond in ammonia show opposite changes. In a metal complex the $\text{C}\equiv\text{N}$ stretching frequency is higher than in the cyanide ion and the frequency of the $\text{C}\equiv\text{N}$ vibration increases with increasing stability of the complex.

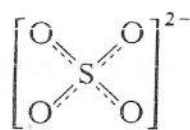
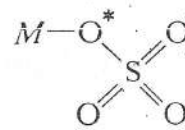
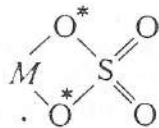
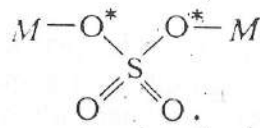
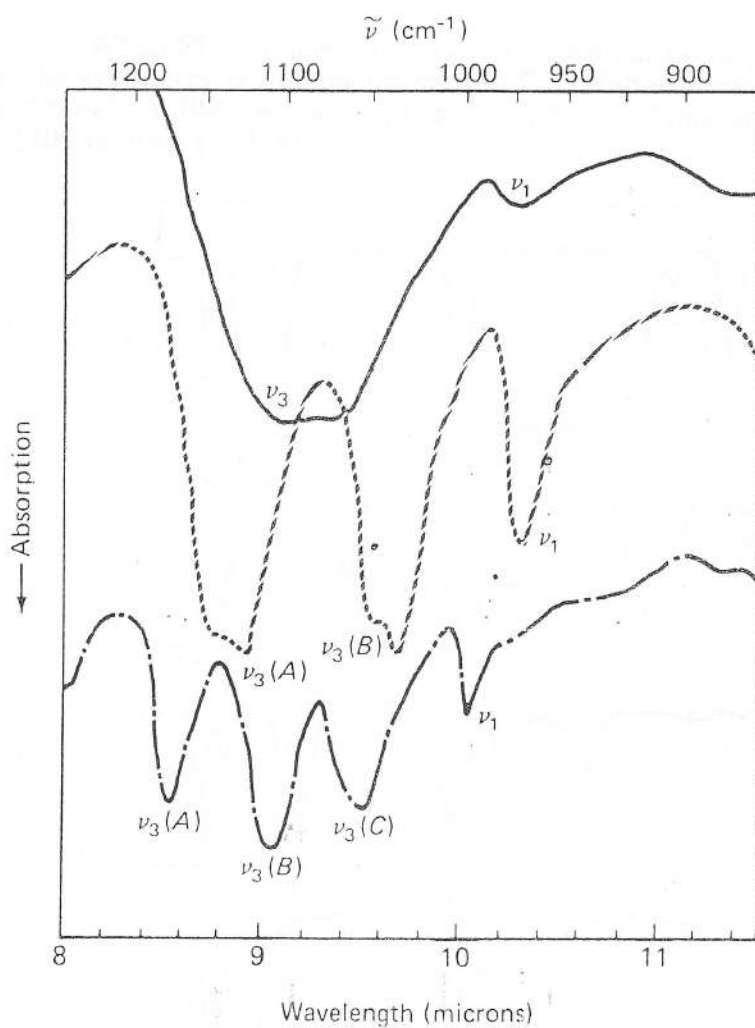
In metal carbonyls, the CO stretching frequency decreases with increasing frequency of the stretching vibration of the $\text{M}-\text{C}$ bond. An increase in the stability of the complex results therefore in a lowering of the strength of the CO bond.

In dimethylglyoxime complexes, the frequency of the $\text{C}=\text{N}$ vibration increases with the decrease of the third ionisation potential of the central atom. The lower frequency of the $\text{C}=\text{N}$ vibration in the chelate ring indicates increased conjugation.

Comparison of the stabilities of acetylacetone complexes and the frequencies of the CO vibration of the carbonyl groups of acetylacetone bound in the complexes shows that the $\text{C}=\text{O}$ bond strength is decreased as the stability of the complexes increases.

Interpretation of IR spectra

IR spectra of sulphate ion

Free ion (T_d)Unidentate (C_{3v})Bidentate (chelating)
 C_{2v} Bidentate (bridging)
 C_{2v} 

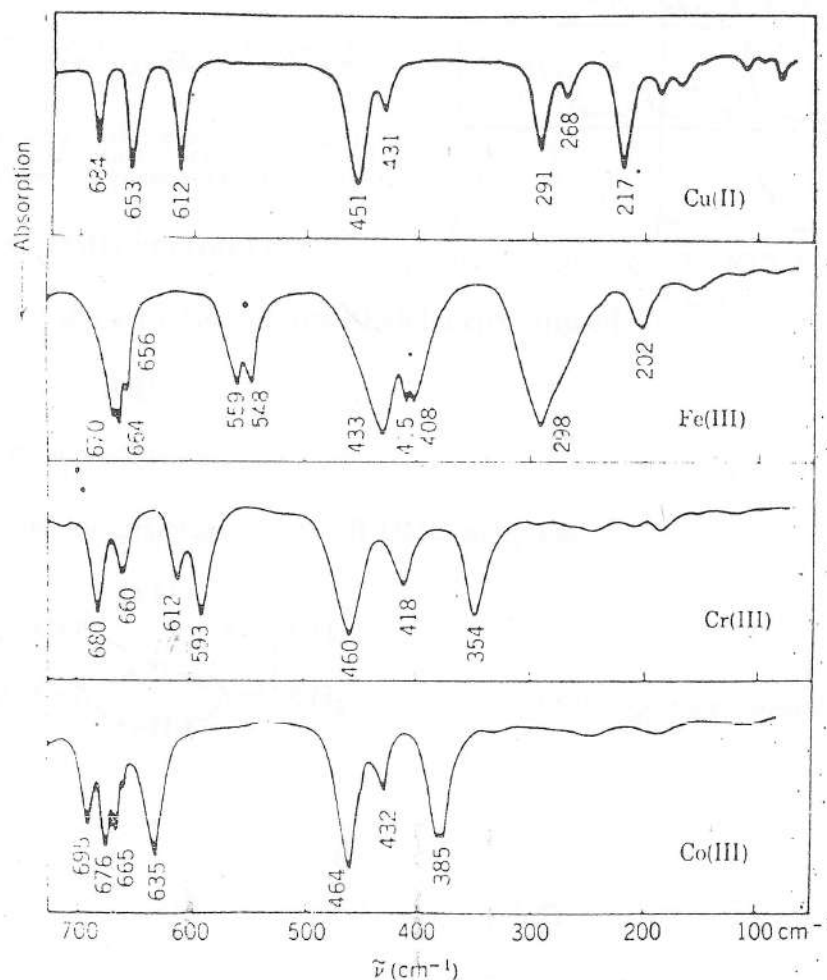
Infrared spectra of: —, $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$; ----, $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$; - · - · -, $[(\text{NH}_3)_4\text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{SO}_4 \end{array} \text{Co}(\text{NH}_3)_4](\text{NO}_3)_3$ (in KBr disk).

1. What are the various ways of coordination for SO_4^{2-} ion and mention their symmetries.
2. Identify the frequencies for the characteristic for SO_4^{2-} ion. There are two bands ν_4 , 1104 cm^{-1} (vs) ν_1 , 973 cm^{-1} (vw).
3. When the SO_4^{2-} ion coordinate to the central metal ion, what is the nature of the ν_1 and ν_3 bands if it behaves

The ν_1 (970 cm^{-1}) band is obtained as a strong band. The ν_4 band undergoes splitting into two bands. They are as the SO_4^{2-} ν_3 band appears in the region 1032 to 1044 cm^{-1} . When the SO_4 ion is coordinated to a metal ion and act as a monodentate ligand, the symmetry of the SO_4^{2-} (T_d) is lowered to C_{3v} . Hence more bands appear.

4. When the SO_4^{2-} ion coordinate to the central metal ion as a bidentate ligand what is the nature of the IR spectrum.

When SO_4^{2-} ion coordinate to the central metal ion as a bidentate ligand, then the symmetry is further lowered to C_{2v} . Hence more bands appear. ν_1 appears very strongly at 995 cm^{-1} and splits into 3 bands. They are in the region 1050 - 1060 (w), 1105 (s) and 1170 (s) cm^{-1} .



. Infrared spectra of bis- and tris(acetylacetonato) complexes.

FIG. 1. Infrared spectra of metal-ethylenediamine complexes in the region 1750—400 cm^{-1} (Hilger H800 spectrometer with NaCl and KBr prisms). The two types of spectrum are designated by A and B. Broken portions of the curves correspond to hexachlorobutadiene mulls, others to Nujol mulls.

[Co(en)₃]Cl₃ (octahedral hydrate): 3510—3440; 3195—3060; 1619; 1591—1563; 1466; 1366; 1325; 1302; 1277; 1251; 1218; 1163—1155; 1122; 1057; 1002; 894; 782; 744; 523—490—465—435 (Type A).

[Cr(en)₃]Cl₃ (octahedral hydrate): 3360; 3190—3060; 2945—2891; 1620; 1574—1544; 1463; 1394; 1359; 1330; 1303; 1275; 1225; 1153—1144; 1115; 1053; 1005; 830—869; 738; 555—530—480—445 (Type A).

[Rh(en)₃]Cl₃ (octahedral hydrate): 3528—3440; 3222—3095; 2697—2773; 1620; 1570; 1460; 1364; 1327; 1306; 1279; 1239; 1215; 1165—1156; 1124; 1057; 879; 793; 751; 723; 578—530—506—465 (Type A).

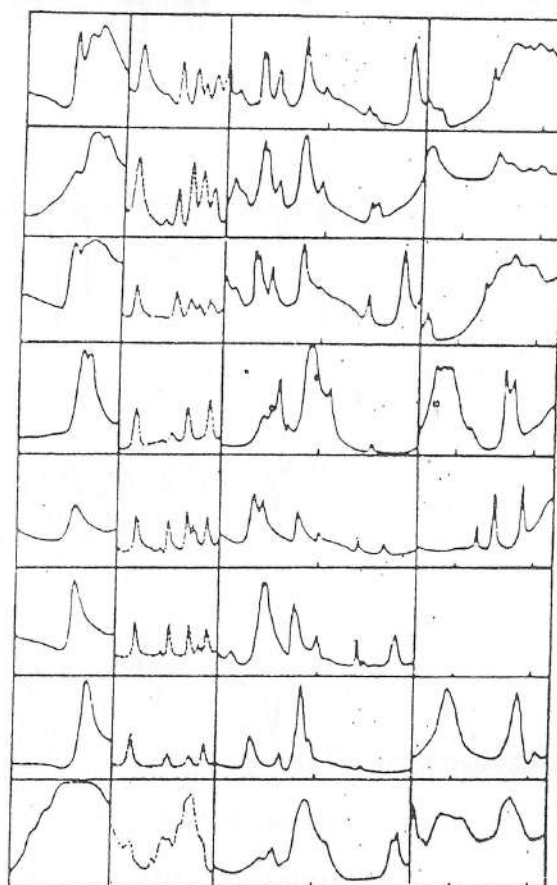
[Ni(en)₃]Cl₃ (octahedral): 3480—3400; 3250; 2940—2875; 1587—1569; 1457; 1393; 1369; 1330; 1275; 1140—1118—1100; 1072; 1026—974; 865; 705—683—662; 522—498 (Type B).

[Pt(en)₃]Cl₃ (planar): 3207—3141—3064; 1610; 1454; 1373; 1326; 1311; 1275; 1154—1128; 1050; 999; 897; 876; 831; 589; 546; 478 (Type A).

[Pd(en)₃]Cl₃ (planar): 3190—3145—3046; 2960—2875; 1601; 1452; 1390; 1367; 1317; 1293; 1273; 1210; 1134—1125; 1055; 997; 894; 875; 798. (Not examined in potassium bromide region) (Type A).

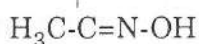
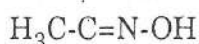
[Cu(en)₃][PtCl₆] (planar): 3562; 3300—3230; 2940—2878; 1633; 1587; 1459; 1365; 1315; 1277; 1162; 1089; 1040—1015; 975; 700; 550 (Type B). *

[M(en)₃][C₂O₄] (tetrahedral): 3505—3425; 3291—3159; 2914—2869; near 1600 broad band; 1455; 1398; 1371; 1303; 1130; 1100; 1021; 791—783; 743; 680—625; 500 (spectrum is complicated by presence of strong oxalate bands, but appears to be of type B).

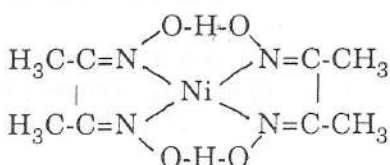


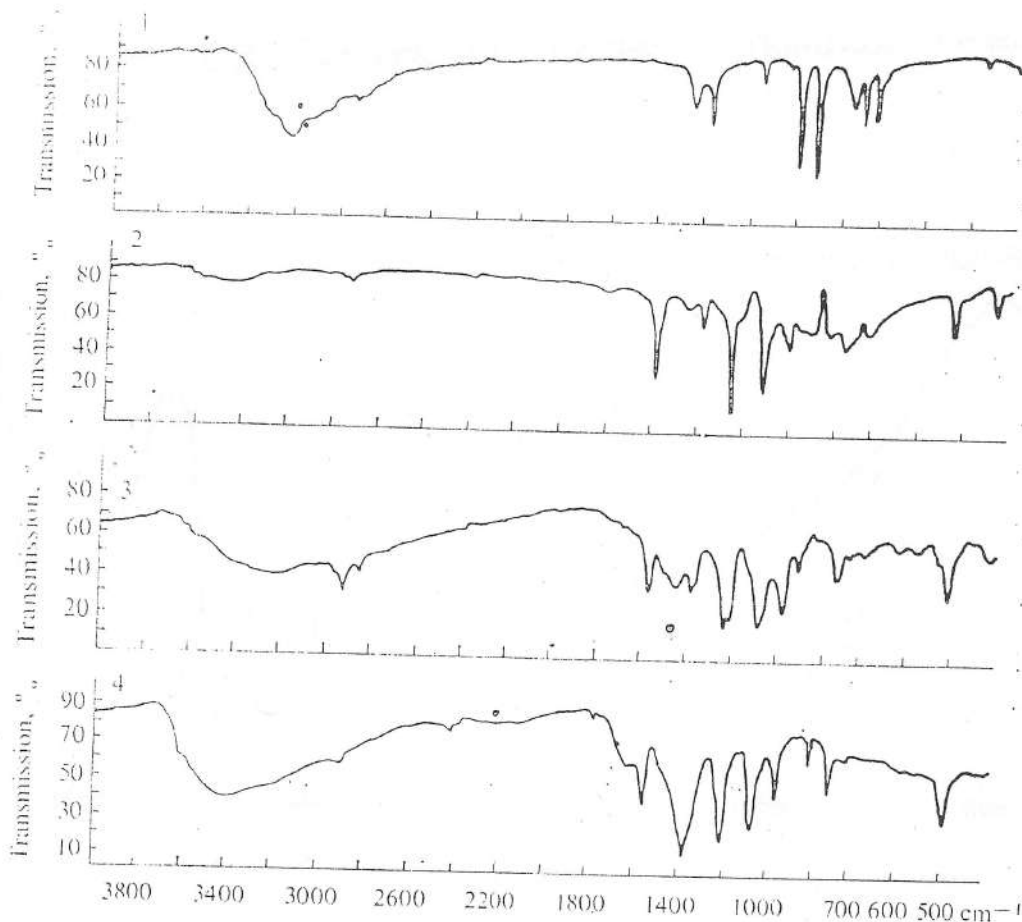
IR spectra of DMG complexes

1. Write the structure of dimethylglyoxime ligand



2. Write the structure of the Ni-DMG complex.





Infrared spectra of 1, dimethylglyoxime and 2, its nickel(II), 3, cobalt(II), 4, cobalt(III), complexes

3. What are the characteristic IR bands for Ni-DMG complex.

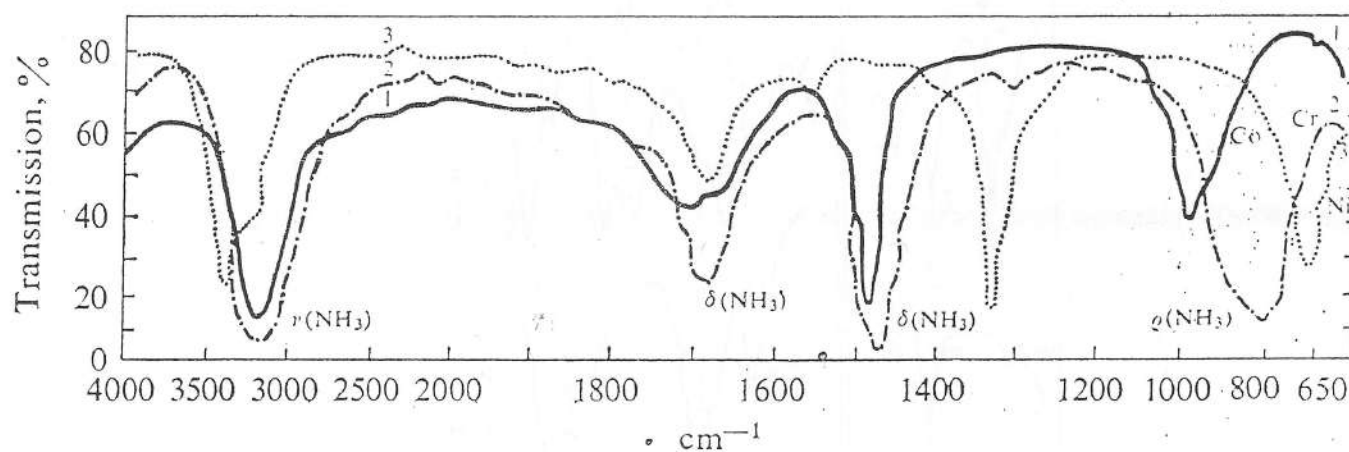
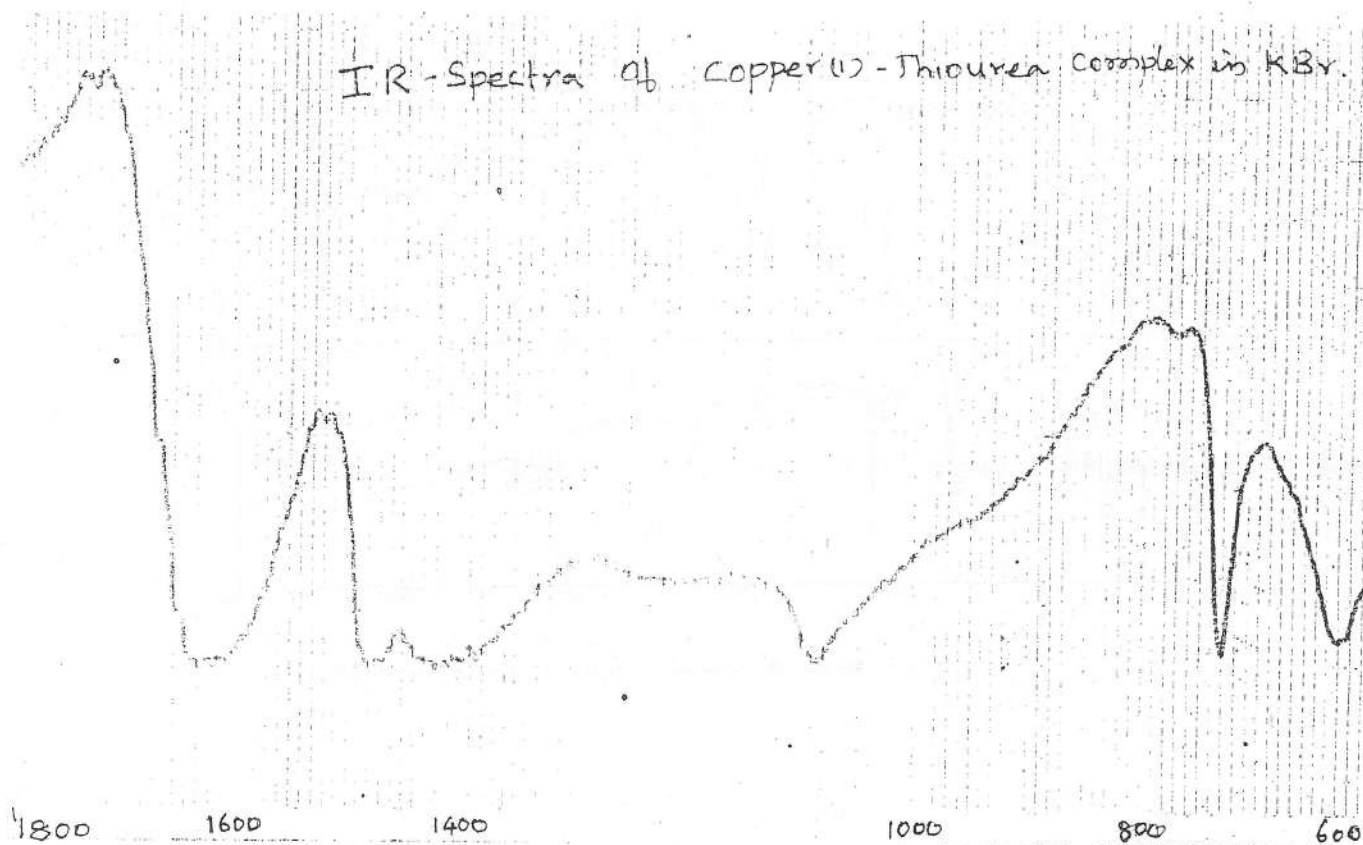
	OH	C=N	N-O	
Ni(II) - DMG	2346	1576	1241	1103 cm ⁻¹

4. What about the position of O-H stretching band in the infrared spectrum of Ni-DMG complex.

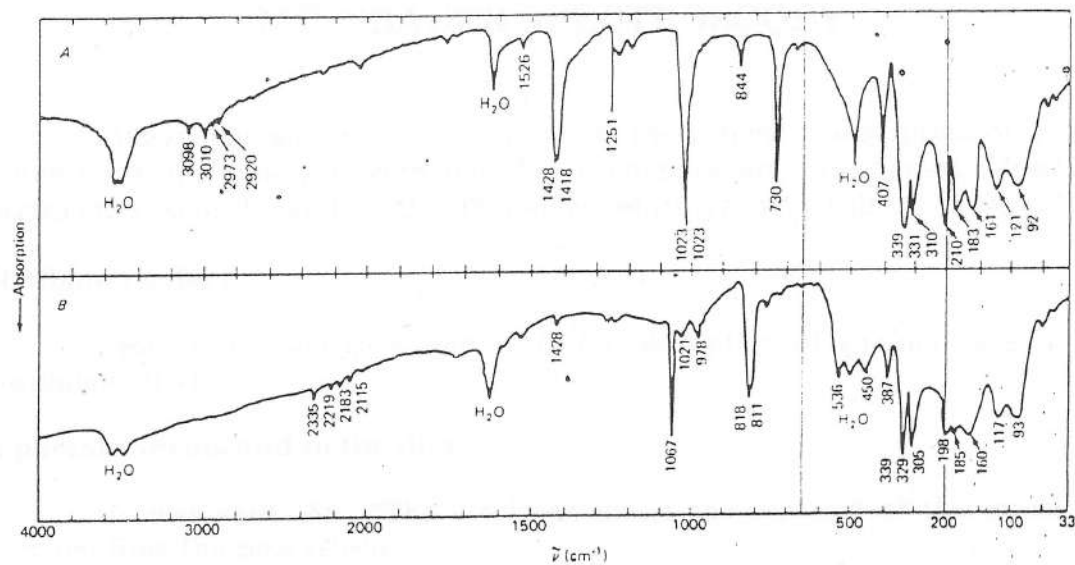
The broad band of low intensity exhibited at 2346 cm⁻¹ is assignable to OH stretching vibration. The same band appears around 3100 cm⁻¹ in the free ligand confirming complexation.

The stretching frequency of CO is 2168 cm⁻¹. The C-O bond order is slightly lower when the CO molecule is coordinated to a metal atom. Consequently, the stretching frequency for such a CO group lies in a slightly lower frequency range 2000 to 2100 cm⁻¹.

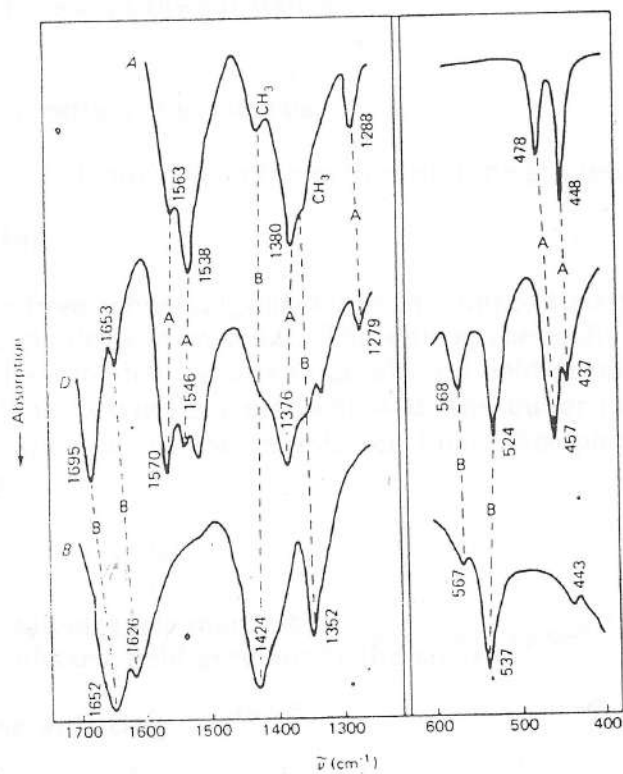
IR - Spectra of Copper(II) - Thiourea complex in KBr.



Infrared spectra of (1) cobalt(III), (2) chromium(III) and (3) nickel(II) hexammine complexes ($650\text{--}4000\text{ cm}^{-1}$)



Infrared spectra of Zeise's salt (A) and Zeise's salt- d_4 (B) from 4000 to 33 cm^{-1} .



Infrared spectra of $\text{K}[\text{Pt}(\text{acac})\text{Cl}_2]$ (A), $\text{Na}_3[\text{Pt}(\text{acac})_2\text{Cl}_2]$ (B) and $\text{K}[\text{Pt}(\text{acac})_2\text{Cl}]$ (D).

MÖSSBAUER SPECTROSCOPY

Mössbauer spectroscopy depends on the resonant absorption of a γ -ray, photon by a nucleus. Although the photon energies are so different, Mössbauer spectra are so sharply resolved that they show splittings comparable to those of NMR.

Mössbauer effect

"Recoil free emission and resonant absorption of gamma rays" is the Mössbauer effect.

Important terms and definitions

Isomer shift (δ) : "The displacement of the centroid of the Mössbauer spectrum from the zero velocity.

$$\delta = KZe^2 \left[\underset{\text{absorber}}{|\psi(o)|^2} - \underset{\text{source}}{|\psi(o)|^2} \right] \times [R_{\text{ex}}^2 - R_{\text{gd}}^2]$$

K = constant characteristic of the substance

Z = atomic number

$e|\psi(o)|^2 = \delta$ electron density at the nucleus.

R_{ex} and R_{gd} = Radius of the nucleus in the excited and the ground state respectively.

Quadrupole splitting

A deviation from spherical geometry in the charge distribution of the atomic nucleus produces a quadrupole moment. The non spherically symmetric charge distribution of the electron shell results in an electric field gradient at the nucleus. The interaction of the electric field gradient with the quadrupole moment of the nucleus effects the splitting of the Mössbauer line. This phenomenon is called quadrupole splitting.

$$\Delta E_Q = \frac{1}{2} e^2 q Q$$

Q = Quadrupole moment

q = electric field gradient at the nucleus.

Magnetic hyperfine splitting

This nuclear effect is analogous to the Zeeman splitting of atomic orbitals by a magnetic field. The magnetic field at the nucleus produced by the surroundings can interact with the nuclear magnetic moment. This interaction causes removal of the degeneracy of nuclear energy levels. The number of different levels obtained from this effect is determined by the magnetic number of the nucleus. In general $(2I + 1)$

levels can be obtained for a given nucleus where I is the nuclear spin quantum number.

Mossbauer spectrum

A plot of the intensity of the gamma rays transmitted through or scattered by the absorber versus the relative velocity of the source-absorber pair is the mossbauer spectrum.

TYPICAL QUESTIONS ON MOSSBAUER SPECTRUM

1. What are the two parameters that are used for obtaining the mossbauer spectrum?

Source velocity (in mm/sec) is plotted against intensity of γ -ray (counts/sec) to obtain mossbauer spectrum.

2. Mention the significance of isomer shift.

The isomer shift depends on a nuclear term dR/R and a chemical term $(1/\psi(0))^2 |\psi(0)|^2$ that gives the difference in the total electron densities at the absorber and source nuclei. If the nucleus in the excited state has a smaller radius than that in the ground state as happens in ^{57}Fe , dR/R is negative and the value of the isomer shift relative to a fixed standard decreases with an increase in the total electron density at the absorber nuclei. On the other hand, if dR/R is positive, as in ^{119}Sn , the values of the isomer shift would increase with an increase in $|\psi(0)|^2$.

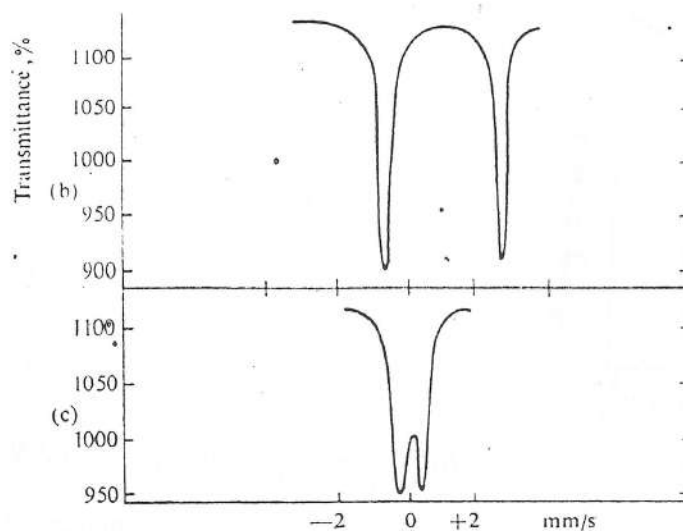
3. What is the information that can be obtained from the magnitude of quadrupole splitting?

The magnitude of the quadrupole splitting can serve as a measure of the inhomogeneity of the electric field of a Mossbauer nucleus. The electric field at the nucleus is determined primarily by the electronic configuration of the atom and consequently by the nature of the bonding, and secondly by the symmetry of the crystal lattice. The occurrence and the magnitude of quadrupole splitting are therefore of use for the study of chemical bonding or the symmetry of the compound.

4. Explain the origin of magnetic hyperfine splitting of ^{57}Fe .

The excited state with $I = 3/2$ is split into four and the ground state with $I = 1/2$ is split into two subsets. Hence six allowed transitions are possible.

A. Mössbauer spectrum of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$



(b) Mössbauer spectrum of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

(c) Mössbauer spectrum of FePO_4

1. What are the parameters that are used for obtaining the Mössbauer spectrum?

Source velocity is plotted against gamma ray counts percentage transmittance.

2. Calculate the isomer shift and ΔE_Q .

$$\begin{aligned}\delta &= 0.13 \\ \Delta E_Q &= 0.315\end{aligned}$$

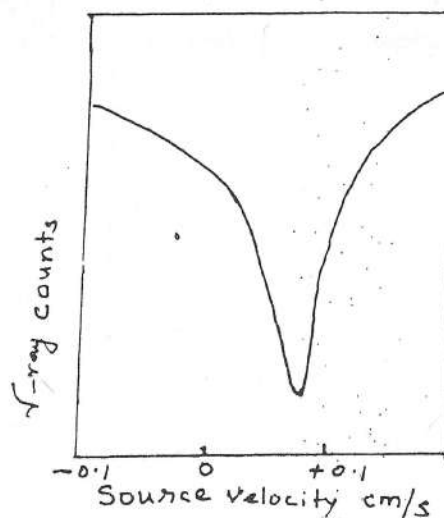
3. Why Mössbauer spectrum of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ shows splitting?

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ has spin free Fe^{2+} ion. It belongs to d^6 system. As a result of the field gradients at the nucleus, quadrupole splitting is observed. Thus it is obvious that, for Fe^{2+} ions containing six d electrons, the s electron density at the nucleus must be lower than for Fe^{2+} ion. Further this compound is a high spin compound and hence Mössbauer spectrum shows quadrupole splitting.

4. What is the significance of positive isomer shift values for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$?

Isomer shift in a positive direction correspond to a decrease in electron density in the region of the nucleus.

B. Mössbauer spectrum of FeCl_3



1. What is the value of isomer shift?

0.085 cm

2. Why there is no quadrupole splitting observed in this spectrum?

FeCl_3 is a spin free complex. Fe^{3+} (d^5) has virtually spherical electric field at the nucleus. In the d^5 case each d orbital has one electron producing a spherical charge distribution. Hence there is no quadrupole splitting.

3. What is the oxidation state of Fe in FeCl_3 .

The oxidation state of Fe in FeCl_3 is +3

4. What is the nature of Cl^- ligand in FeCl_3 ?

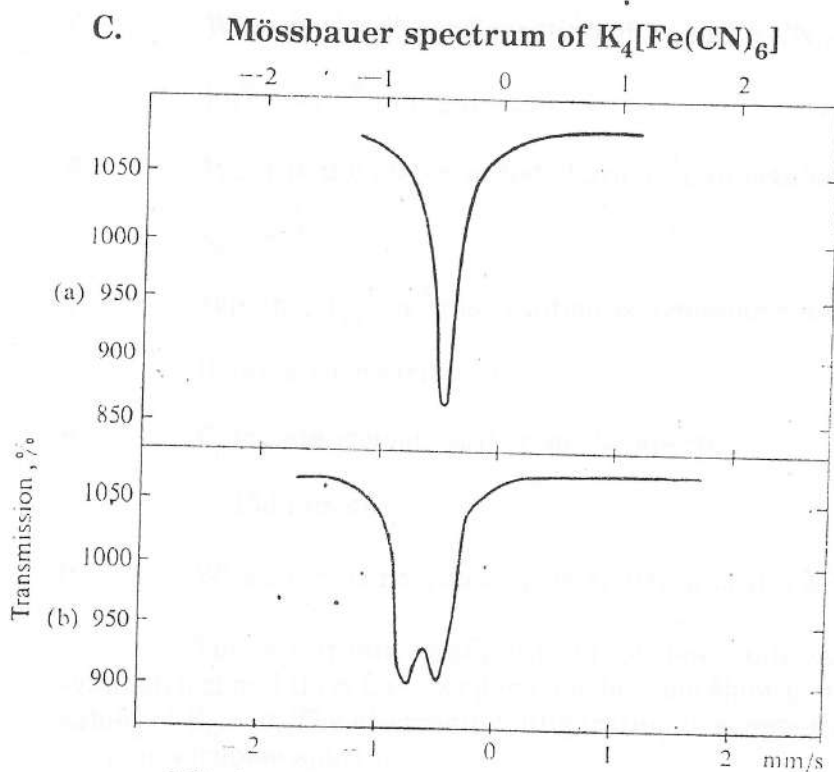
Cl^- ligand is found in the lower end of the spectrochemical series. hence it is a weak ligand.

5. How many d^n electrons are there in Fe^{3+} ?

There are six electrons in d orbitals, d^6 .

6. What is the nature of electron distribution in octahedral field?

$t_{2g}^3 e_g^2$ hence it has symmetric distribution and hence there is no quadrupole splitting.



Mössbauer spectra of iron-cyanide complexes
(a) $K_4[Fe(CN)_6] \cdot 3H_2O$, (b) $K_3[Fe(CN)_6]$

- What is the oxidation state of iron in $[Fe(CN)_6]^{4-}$?

$$x + 6(-1) = -4$$

$$x = 6 - 4 = 2$$
- What is the geometry of $[Fe(CN)_6]^{4-}$?
 Octahedral geometry.
- What is the position of CN^- in spectrochemical series?
 CN^- ligand is found in the higher end of the spectrochemical series.
- Whether $K_4Fe(CN)_6$ is spin free complex or spin paired complex?
 Spin paired complex.

5. What is the d^n configuration of Fe in $\text{Fe}(\text{CN})_6^{4-}$?

Fe^{2+} has d^6 configuration.

6. What is the electron distribution in an octahedral field?

$t_{2g}^6 e_g^0$

7. Whether $t_{2g}^6 e_g^0$ distribution is symmetric or unsymmetric distribution.

Symmetric distribution.

8. Calculate isomer shift from the spectra.

-0.333 mm/sec.

9. Why there is no quadrupole splitting in the Mossbauer spectrum?

The electronic configuration of low spin octahedral Fe^{2+} complex is symmetrical and therefore its spectrum does not show quadrupole splitting. Hence the value of $E_Q = 0$. The electronic configuration is symmetric. ($t_{2g}^6 e_g^0$) and hence there is no quadrupole splitting.

D. Mössbauer spectrum of $\text{K}_3[\text{Fe}(\text{CN})_6]$

1. What is the oxidation state of Fe in $\text{K}_3[\text{Fe}(\text{CN})_6]$?

2. How many d electrons are there in Fe^{3+} ?

There are five electrons in d orbital and hence it belongs to d^5 system.

3. What is the nature of CN^- ligand?

It is found in the higher end of the spectrochemical series. Hence it is a stronger ligand.

4. What is the co-ordination geometry of $\text{Fe}(\text{CN})_6^{3-}$?

Octahedral geometry.

5. Whether $\text{K}_3\text{Fe}(\text{CN})_6$ is a spin free complex or spin paired complex.

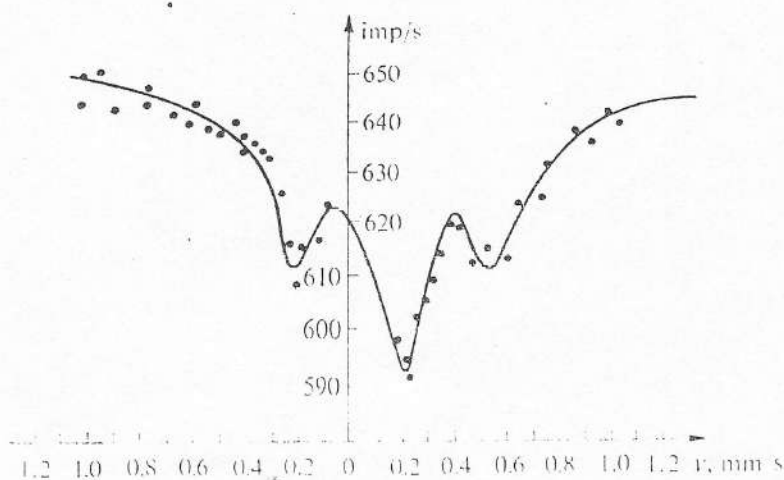
Spin paired complex.

6. What is the d electron distribution in $\text{Fe}(\text{CN})_6^{3-}$?

$t_{2g}^5 e_g^0$. Hence it is a symmetrical distribution.

7. Calculate isomer shift of K_3FeCZ_6
- 0.413 mm/sec.
8. What is the nature of Mossbauer line for $K_3(FeCN_6)$?
Mossbauer spectrum exhibit quadrupole splitting.
9. What is the reason for quadrupole splitting?
Five electrons are accommodated in the 3d (t_{2g}) electron shell of low spin iron -III complexes. This electronic configuration gives rise even in complexes of regular octahedral geometry to a small quadrupole splitting.
10. What is the value of ΔE_q , quadrupole splitting?

$$\Delta E_q = 0.373 \text{ mm/sec.}$$



Mössbauer spectrum of iron(II) dimethylglyoxime
with the composition $Na_2Fe_3(dmg)_6(OH)_2$