

İzmir Institute of Technology

Faculty of Science

Department of Chemistry

CHEM 304

INORGANIC CHEMISTRY

LABORATORY MANUAL

Spring Term

2007

Introduction

This manual has been prepared for CHEM 304 Inorganic Chemistry Laboratory and includes the experiments, which are related to the topics covered in CHEM 302 Inorganic Chemistry II course. The main purpose of this laboratory is to provide the students an appreciation for the synthesis and characterizations of inorganic complexes. It is also aimed to provide the students a degree of competence in the laboratory skills required for accurate and precise chemical analysis. Therefore it is expected that the students will demonstrate proficiency in the theory underlying analytical techniques and to apply this theory to obtain reliable analytical results on the synthesis of inorganic complexes.

Course Policies and Information

In this laboratory, you will be working as a team with two or three person in each group. During the first lab period your instructor will assign you to a group. You will then introduce yourself to group members and get to know other members of your group. Then your instructor will read you important safety rules. In this meeting of the laboratory, you will also be given your first lab experiment and the rest of this lab period you will work on a plan of action for the first experiment.

Each student in the group must have a lab Notebook and bring it to the lab every week. You should keep a good notebook with all the calculations and the results because your instructor will grade your Lab notebooks at the end of the each experiment. Finally, each member of your group has to write a 5 or 6 page lab report after completing the experiment. This is going to be a individual report therefore, even if your results are the same. The reports you write must be your own work. If your instructor finds out that your report is exactly the same with another member of your group, you will not receive any credit for that report and he/she may consider it as cheating.

Typical grading scheme for a project is given below.

Quiz	40%
Lab Notebook	50%
Participation	10%

Your overall grade from lab performance will be calculated by taking the sum of your all experiments. There will also be a final exam at the end of the semester. Your final grade for

the lab will be obtained by adding 70% of your overall lab performance grade and 30% of your final lab exam.

Attendance is required and you are expected to attend all scheduled laboratory sessions. **If you miss more than two-lab session without a valid reason you will be automatically dropped from lab.** Should you be sick and can not come to lab, you need to bring a doctor's excuse from "UNIVERSITY HEALTH CENTRE". Remember this is a group work and if you can not be there inform other members of your group. Please be also on time since your group members will depend on you to start the experiments.

Format of the Lab Report

You should prepare your lab reports by handwriting. They should include tables and illustrations where necessary. Typically, a lab report should contain the following sections: **title page, introduction, experimental section, results and discussion, and references.**

Your title page should be a separate page including the title of the project which might simply be the name of the experiment, your name, name of the course and the date the report is due.

Safety Rules

The chemistry laboratory is not a dangerous place to work as long as all necessary precautions are taken seriously. In the following paragraphs, those important precautions are described. Everyone who works and performs experiments in a laboratory must follow these safety rules at all times. Students who do not obey the safety rules will not be allowed to enter and do any type of work in the laboratory and they will be counted as absent. It is the student's responsibility to read carefully all the safety rules before the first meeting of the lab.

Eye Protection: Because the eyes are particularly susceptible to permanent damage by corrosive chemicals as well as flying objects, safety goggles must be worn at all times in the laboratory. Prescription glasses are not recommended since they do not provide a proper side protection. No sunglasses are allowed in the laboratory. Contact lenses have potential hazard because the chemical vapors dissolve in the liquids covering the eye and concentrate behind the lenses. If you have to wear contact lenses consult with your instructor. If possible try to wear a prescription glasses under your safety goggles. In case of any accident that a chemical splashes near your eyes, immediately wash your eyes with lots of water and inform your instructor. Especially, when heating a test tube do not point its mouth to anyone.

Always assume that you are the only safe worker in the lab. Work defensively. Never assume that everyone else is as safe as you are. Be alert for other's mistakes.

Cuts and Burns: Remember you will be working in a chemistry laboratory and many of the equipment you will be using are made of glass and it is breakable. When inserting glass tubing or thermometers into stoppers, lubricate both the tubing and the hole in the stopper with water. Handle tubing with a piece of towel and push it with a twisting motion. Be very careful when using mercury thermometer. It can be broken easily and may result with a mercury contamination. Mercury vapor is an extremely toxic chemical.

When you heat a piece of glass it gets hot very quickly and unfortunately hot glass looks just like a cold one. Handle them with a tong. Do not use any cracked or broken glass equipment. It may ruin an experiment and worse, it may cause serious injury. Place it in a waste glass container. Do not throw them into the wastepaper container or regular waste container.

Poisonous Chemicals: All of the chemicals have some degree of health hazard. Never taste any chemicals in the laboratory unless specifically directed to do so. Avoid breathing toxic vapors. When working with volatile chemicals and strong acids and bases use ventilating hoods. If you are asked to taste the odor of a substance do it by wafting a bit of the vapor toward your nose. Do not stick your nose in and inhale vapor directly from the test tube. Always wash your hands before leaving the laboratory.

Eating and drinking any type of food are prohibited in the laboratory at all times. Smoking is not allowed. Anyone who refuses to do so will be forced to leave the laboratory.

Clothing and Footwear: Everyone must wear a lab coat during the lab and no shorts and sandals are allowed. Students who come to lab without proper clothing and shoes will be asked to go back for change. If they do not come on time it will be counted as an absence. Long hair should be securely tied back to avoid the risk of setting it on fire. If large amounts of chemicals are spilled on your body, immediately remove the contaminated clothing and use the safety shower if available. Make sure to inform your instructor about the problem. Do not leave your coats and back packs on the bench. No headphones and Walkman are allowed in the lab because they interfere with your ability to hear what is going on in the Lab.

Fire: In case of fire or an accident, inform your instructor at once. Note the location of fire extinguishers and, if available, safety showers and safety blankets as soon as you enter the laboratory so that you may use them if needed. Never perform an unauthorized experiment in the laboratory. Never assume that it is not necessary to inform your instructor for small accidents. Notify him/her no matter how slight it is.

Laboratory Care and Waste Disposal

Remember that the equipment you use in this laboratory will be used by many other students. Please leave the equipment and all workspaces as you wish to find them. After the end of the each lab, clean off your work area. Wash your glassware. When weighing any material on the balances, do not weigh directly onto the balance pan. Weigh your material on a piece of weighing paper. The balances are very sensitive instruments and should be treated with great care.

If you take more reagents than you need, do not put excess back into the bottle. It may be contaminated. Treat it as waste and dispose of it accordingly. It is most likely that, during any experiment you will perform, you will generate some waste chemicals and solutions to dispose of. Never put them down the sink unless specifically told to do so by your instructor. There will be inorganic, organic, and solid waste containers in the lab. Dispose of your waste in appropriate container.

Experiment. 1 HEXAAMMINE COBALT(III) CHLORIDE

Purpose:

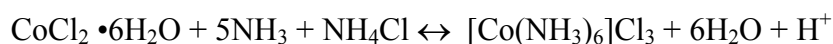
This experiment illustrates the formation of a coordination compound of cobalt. It raises the question of whether or not chlorine atom is coordinated to cobalt.

Introduction:

The purpose of this experiment was to synthesize a 6-coordinate cobalt(III) compound from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. This is made difficult by the fact that Co^{2+} ion is more stable than Co^{3+} for simple salts. There are only a few salts of cobalt(III), such as CoF_3 , that are known. However, cobalt(III) can be made stable when in octahedrally coordinated compounds..

The determination as to whether or not the chlorine atom is coordinated or ionic can be determined by gravimetric determination of the chloride precipitated with silver ions. Volumetric determination of the chloride with silver is difficult because the usual indicators do not work. Volumetric determinations have been done using mercury(II) nitrate. Because mercury(II) chloride is only slightly ionized, there are very few mercury(II) ions in solution as long as there are chloride ions present. The excess mercury(II) ions at the end point can be detected by using sodium nitroprusside as an indicator. The mercury(II) nitroprusside which forms the excess mercury(II) ions is insoluble and separates as a white turbidity.

A difficulty in this experiment is the oxidation of cobalt(II) to cobalt(III). This could be accomplished through the addition of hydrogen peroxide, but this method is not suitable for this experiment. A more suitable method is the air oxidation of cobalt with carbon as a catalyst. An additional benefit of carbon as a catalyst is its ability to shift the equilibrium in favor of the desired product.



Experimental Procedure

Preparation of Hexaamminecobalt(III) chloride

Add 5.0g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 3.3 g of NH_4Cl to 30 mL of DI water in a 250-mL Erlenmeyer flask. In the hood add 1.0 g activated charcoal and 45mL conc. aqueous ammonia. Cool the brown slurry in an ice bath to 0°C , then add 4.0 mL 30% H_2O_2 from a buret. Do not allow the temperature to rise above 10°C . Heat the resulting red-brown solution to 60°C , and maintain this temperature for 30min. (The incubation is needed to ensure complete displacement of all aqua ligands.) Cool the mixture to 0°C ; the product will precipitate from the solution. Collect the product and the charcoal by filtration. Recrystallization is necessary to separate the product from the activated charcoal. Place the solid in a 250-mL Erlenmeyer flask, and add 40 mL hot water and 1.0 mL conc. HCl (test the solution with litmus if necessary, add a few more drops of HCl) . Heat the mixture to 70°C , and filter while still hot. Place the filtrate in an ice bath, and add 1.0 mL cold conc. HCl (it may be precipitated by common-ion effect). Collect the orange solid by filtration, wash with 25 mL ice-cold ethanol, and allow to air-dry.

Experiment 2. CHLOROPENTAAMMINECOBALT(III) CHLORIDE

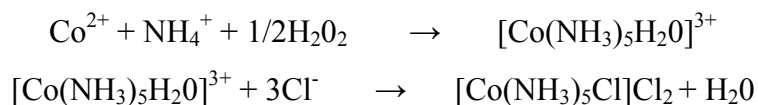
Purpose:

The purpose is to synthesize chloropentaamminecobalt(III) chloride. It raises the question of whether the chloride atom is coordinated to cobalt or not.

Introduction:

The cobalt 2+ ion is more stable than the cobalt 3+ ion for simple salts of cobalt. Only a few salts of Co(II) such as CoF_3 are known. However, complexation stabilizes the higher oxidation state, and a number of very stable octahedrally coordinated complexes of cobalt(III) are known.

The equations of the preparation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ are written :



Experimental Procedure:

Preparation of Chloropentaamminecobalt (III) chloride

In a fume hood, add 5 g of ammonium chloride to 30 mL concentrated aqueous ammonia in a 250-mL Erlenmeyer flask. (The combination of NH_4Cl and $\text{NH}_3(\text{aq})$ guarantees a large excess of the NH_3 ligand.) Stir the ammonium chloride solution vigorously using a magnetic stirring plate while adding 10 g finely divided $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in small portions. Next, add 8 mL 30% hydrogen peroxide to the brown Co slurry, using a buret that has been set up in the hood and filled by the laboratory instructor. An addition rate of about 2 drops per second is usually sufficient, but care should be taken to avoid excessive effervescence in this exothermic reaction. (If the reaction shows signs of excessive effervescence, turning off the magnetic stirrer momentarily will usually prevent overflow of the solution.) When the effervescence has ceased, add 30 mL conc. HCl with continuous stirring, pouring about 1-2 mL at a time. At this point, the reaction may be removed from the hood. Use a heater to heat the solution to 60°C with occasional stirring. Hold the temperature between 55°C and 65°C for 15 min.; this incubation period is necessary to allow complete displacement of all aqua ligands. Add 25 mL distilled water, and allow the solution to cool to room temperature. Collect the purple product by filtration through a Buchner funnel; wash it three times with 7.5 mL cold distilled water and twice with 7.5 mL ice-cold ethanol. (The solutions must be cold to prevent undue loss of product by redissolving.) Transfer the product to a crystallizing dish, loosely cover with aluminum foil, and allow to dry until the following laboratory period.

Experiment 3. WERNER THEORY

Purpose:

The aim of this experiment is to determine the molar conductance of $[\text{Co}(\text{NH}_3)_5]\text{Cl}_3$, and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ by measuring conductivity of these compounds.

Introduction:

In ionic compounds of the main group elements, it is usually a trivial matter to deduce the number of ions per mole present in infinitely dilute solution. The ionic compounds are viewed as dissociating completely in the dilute solution (although as the concentration of solute rises, the degree of ionization changes drastically), and thus $\text{Ca}(\text{NO}_3)_2$ would be expected to consist of three ions: one Ca^{2+} ion and two nitrate (NO_3^-) ions.

In transition metal complexes, the situation is not nearly as simple. A given anion may be a part of the complex (in which case it generally does not dissociate) or it may be present as a counterion (in which case it does). Werner, in 1912, investigated the octahedral complex $\text{Co}(\text{en})_2\text{Cl}_3$ (en = ethylenediamine) which have three different potential ligand arrangements in aqueous solution:

$[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}_3$	4 ions
$[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$	3 ions
$[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$	2 ions

There is no way of knowing in advance which of the above formulas is correct (The situation is complicated further in that optical activity is also possible in the above case.) The number of ions constituting the complex is best determined by measuring the conductivity of the solution of that compound. This conductivity measurement allows one to tell how many ions (cations and anions) are present in solution when an ionic product is dissolved in water.

Those ionic compounds that are soluble in water and conduct electric current in aqueous solution are called **electrolytes**. The dissolution process consists of complete dissociation of ionic compounds into mobile cations and anions. There are many compounds, which though soluble in water, do not exhibit any conductivity. These are termed nonelectrolytes. There is still another group of compounds that exhibit conductance in solutions only when that solution is quite dilute. Such compounds are known as weak electrolytes. Solutions that contain large numbers of mobile ions (cations and anions from the

soluble ionic compounds) conduct current well, and solutions that contain only a few ions (acetic acid) or relatively immobile ions show poor conductivity.

The conductivity of a solution varies with the number, size, and charge of the ions constituting the solution. The viscosity of a solution also affects the conductivity, by affecting the mobility of the ions. Ions of different species in solution will therefore show different conductivities. If, by means of a chemical reaction, we replace one ionic species by another having a different size and/or charge, we would observe a corresponding change in conductivity of the resulting solution.

The conductivity, L , of a solution is presented by the equation

$$L = Bc_i\alpha_iZ_i$$

where B is a constant that depends on the size and the geometry of the conductance cell, c_i is the concentration of individual ions in solution, α_i is the equivalent ionic conductance of individual ions, and Z_i is the charge of the ions.

In practice, although the conductance of a solution is more useful in dealing with electrolyte solutions, it is the resistance of a solution that is experimentally measured. The conductance is calculated from the resistance. The resistance of a solution is determined by inserting two electrodes into a solution. The resistance, R , is proportional to the distance, d , between the two electrodes and inversely proportional to the cross-sectional area, A , of the solution enclosed between the electrodes.

$$R = \rho.d / A$$

The term ρ is called the **specific** resistance or more simply, the **resistivity**. The ratio d/A is usually referred to as the **cell constant**, K . Thus the above relation becomes

$$R = K.\rho$$

The **conductance**, L , of a solution is defined as the reciprocal of the specific resistance.

$$k = 1/\rho = (d/A)(1/R) = K.L$$

In practice, the cell constant, K , is determined for any cell by measuring the conductivity of a 0.0200M KCl solution at 25 °C, for which the specific conductivity, k , is 0.002 768 ohm⁻¹.

The total conductivity of a solution arises from several sources, the largest of which is

the ions. The self-ionization of a solvent contributes as well, but in practice is small enough to be neglected in all but the most careful measurements.

A very useful quantity is the **equivalent conductivity**, Λ . It is defined as the value of the specific conductivity, k , contributed by one equivalent of ions of either charge. More specifically, it is defined as the conductance of a solution containing one gram-equivalent of an electrolyte placed between electrodes separated by a distance of 1 cm. If c is the concentration of the solution in gram-equivalents per liter, the volume of the solution in cubic centimeters per equivalent (cm^3/equiv) is equal to $1000/c$. The equivalent conductance, Λ , is then given by

$$\Lambda = \frac{1000.k}{c}$$

Substituting for k ,

$$\Lambda = \frac{1000.LK}{c}$$

Another frequently used quantity in conductance measurements is the **molar conductance**, Λ_m , defined as the conductance of a one cubic centimeters volume of solution that contains one mole (or formula weight) of the electrolyte. If M is the concentration of the solution in moles per liter, then the volume in cubic centimeters per mole is $1000/M$. The molar conductance is then given by

$$\Lambda_m = \frac{1000.k}{M}$$

By comparing the molar conductance measured for a particular compound with that of

a known ionic compound, we can estimate the number of ions produced in a solution. A range of values of molar conductance for 2-5 ions at 25 °C in water is given below.

Number of ions	Molar Conductance (<u>cm⁻¹mol⁻¹ohm⁻¹</u>)
2	118-131
3	235-273
4	408-435
5	~560

The equivalent conductivity increases with increasing dilution due to the lessened interionic forces between ions (less ion pairing is the classical way of stating this).

Experimental Procedure:

Conductivity measurements require the use of two instruments: the conductivity cell and the conductivity meter or bridge. The cell constant, K , is first determined by measuring the conductivity, L , of an accurately prepared 0.0200M KCl solution for which the value of specific conductivity, k , is known to be 0.002768 ohm⁻¹

$$K = k/L$$

The molar conductivity of any compound is determined in the following way.

1. A 1×10^{-3} M solution of the compound of interest is prepared.
2. The conductivity is measured in the same cell for which the cell constant has been previously determined, as described previously.
3. The cell should be rinsed before each measurement.

Experiment 4. POTENTIOMETRY

Purpose:

The aim of this experiment is to determine the number of chloride ions in the $[\text{Co}(\text{NH}_3)_5]\text{Cl}_3$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

Introduction:

There are a lot of quantification methods to find the ions to be found first and second effect area in the coordination compounds. Generally argentometric titrations are preferred due to the chloride ions in the coordination compounds. However, the indicator such as CrO_4^{2-} or flossein should be used in the determination of chloride ions. CrO_4^{2-} indicator changes the color to the tile red, and flossein indicator changes the color to the rose pink at the end of the titration. Due to the colorful solutions of complexes, determination of the end point of a titration is difficult. Therefore an instrument should be used to obtain the end point. Potentiometer will be used for the purpose of the titration, due to its applicability. Potentiometric titrations provide data that are more reliable than data from titrations that use chemical indicators and are particularly useful with colored or turbid solutions and for detecting the presence of unsuspected species.

A potentiometric titration involves measurement of the potential of a suitable indicator electrode as a function of titrant volume. The information provided by a potentiometric titration is not the same as that obtained from a direct potentiometric measurement.

Several methods can be used to determine the end point of a potentiometric titration. The most straightforward involves a direct plot of potential as a function of reagent volume, as in Figure 1(a) the midpoint in the steeply rising portion of the curve is estimated visually and taken as the end point. Various graphical methods have been proposed to aid in the establishment of the midpoint, but it is doubtful that these procedures significantly improve its determination.

A second approach to end-point detection is to calculate the change in potential per unit volume of titrant (that is, $\Delta E/\Delta V$), as in column 3 of Table 1.1. A plot of these data as a function of the average volume V produces a curve with a maximum that corresponds to the

point of inflection (Figure 1(b)). Alternatively, this ratio can be evaluated during the titration and recorded in lieu of the potential. Inspection of column 3 of Table 1.1 reveals that the maximum is located between 24.30 and 24.40 ml; 24.35 ml would be adequate for most purposes.

Column 4 of Table 1.1 and Figure 1(c) show that the second derivative for the data changes sign at the point of inflection. This change is used as the analytical signal in some automatic titrators.

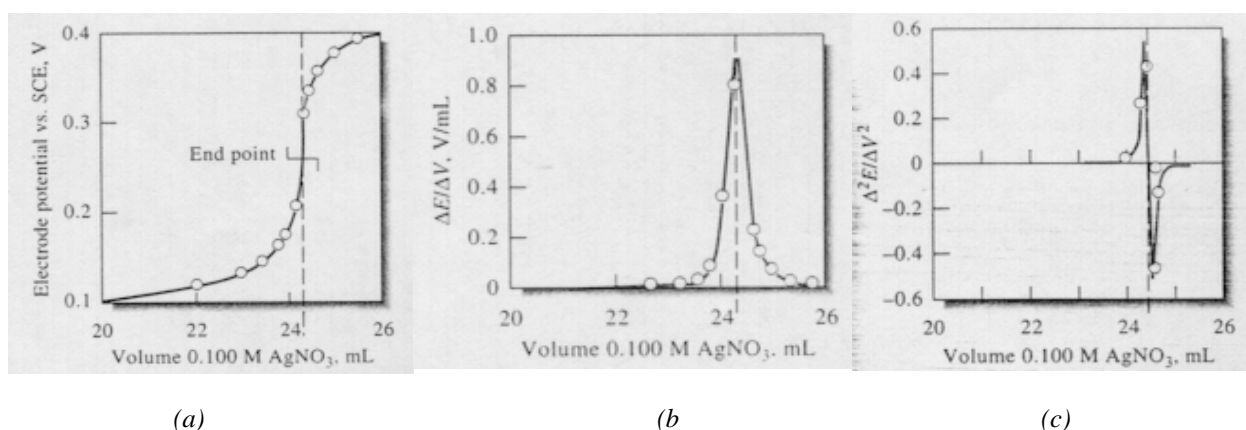


Figure 1 Titration of 2.433 mmol of chloride ion with 0.10000 M silver nitrate. (a) Titration curve; (b) First-derivative curve; (c) Second-derivative curve.

Table 1 Potentiometric Titration Data For 2.433 mmol of Chloride with 0.1000 M Silver Nitrate

Volume AgNO ₃ , mL	<i>E</i> vs. SCE, V	$\Delta E/\Delta V$, V/mL	$\Delta^2 E/\Delta V^2$, V ² /mL ²
5.0	0.062	0.002	
15.0	0.085	0.004	
20.0	0.107	0.008	
22.0	0.123	0.015	
23.0	0.138	0.016	
23.50	0.146	0.050	
23.80	0.161	0.065	
24.00	0.174	0.09	
24.10	0.183	0.11	
24.20	0.194	0.39	2.8
24.30	0.233	0.83	4.4
24.40	0.316	0.24	-5.9
24.50	0.340	0.11	-1.3
24.60	0.351	0.07	-0.4
24.70	0.358	0.050	
25.00	0.373	0.024	
25.5	0.385	0.022	
26.0	0.396	0.015	
28.0	0.426		

All the foregoing methods of end-point evaluation are predicated on the assumption that the titration curve is symmetric about the equivalence point and that the inflection in the curve corresponds to this point. This assumption is perfectly valid, provided the participants in the titration react with one another in an equi-molar ratio and also provided the electrode reaction is perfectly reversible. The former condition is lacking in many oxidation/reduction titrations; the titration of iron (II) with permanganate is an example. The curve for such titrations is ordinarily so steep; however, that failure to account for asymmetry results in a vanishingly small titration error.

Silver nitrate is without question the most versatile reagent for precipitation titrations. A silver wire serves as the indicator electrode. For reagent and analyte concentrations of 0.1 M or greater, a calomel reference electrode can be located directly in the titration vessel without serious error from the slight leakage of chloride ions from the salt bridge. This leakage can be a source of significant error in titrations that involve very dilute solutions or require high precision, however. The difficulty is eliminated by immersing the calomel electrode in a potassium nitrate solution that is connected to the analyte solution by a salt bridge containing potassium nitrate. Reference electrodes with bridges of this type can be purchased from laboratory supply houses.

A theoretical curve to a potentiometric titration is readily derived. For example, the potential of a silver electrode in the argentometric titration of chloride can be described by;

$$E_{\text{Ag}} = E^0_{\text{AgCl}} - 0,0592 \log [\text{Cl}^-] = 0,222 - 0,0592 \log [\text{Cl}^-]$$

where E^0_{AgCl} , is the standard potential for the reduction of AgCl to Ag(s). Alternatively, the standard potential for the reduction of silver ion can be used:

$$E_{\text{Ag}} = E^0_{\text{AgCl}} - 0,0592 \log \frac{1}{[\text{Ag}^+]} = 0,799 - 0,0592 \log \frac{1}{[\text{Ag}^+]}$$

The former potential is more convenient for calculating the potential of the silver electrode when an excess of chloride exists, whereas the latter is preferable for solutions containing an excess of silver ion. Potentiometric measurements are particularly useful for titrations of mixtures of anions with standard silver nitrate.

Experimental Procedure:

1. Weight 0.1–0.2 gram of complexes then solve in 10 ml water.
2. Fill the burette 0.1 M of AgNO_3 solution
3. Read the potential of the solution after adding 0.5 ml of AgNO_3 solution
4. Find the end point of the titration and calculate the numbers of chlorides that are not in the coordination sphere.
5. Again weight 0.1–0.2 gram of complexes into the 100 mL of beaker then dry the complexes by the helping of 7–8 mL 1 M NaOH. In this procedure the complexes are decomposed. Repeat the steps 1 to 4 again. At the end of the titration the total number of chlorides in the complexes will be determined.
6. The difference between the number of chlorides in the step 5 and 6 gives the number of chlorides that are found in the primary coordination sphere.

Experiment 5. SYNTHESIS of trans-dichlorobis (ethylenediamine) cobalt (III) Chloride

Purpose:

The purpose of this experiment synthesize trans-dichlorobis (ethylenediamine) cobalt (III) Chloride.

Introduction:

The modern area of inorganic chemistry can be said to have begun at the turn of the 20th century with Alfred Werner's pioneering work on metal complex structure and coordination. Werner proved that compounds containing six ligands connected to a central metal atom were indeed octahedral by an elegant resolution of the complex $[(\text{Co}(\text{en})_2(\text{NH}_3)\text{X})]^{2+}$. This type of geometry had been theorized earlier (1875) by van't Hoff, who suggested that appropriately substituted octahedral molecules should exhibit geometric isomerism.

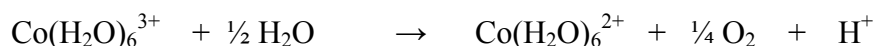
Compounds having the same formulas but different structures are isomeric. With geometrical isomers, it is the arrangement of ligands on the central atom that differs. In an octahedral compound of formula MA_4B_2 (M = metal, A and B = ligand), where a central metal is surrounded by four of one type of ligand and two of another, there are two ways to arrange the groups, as shown in Figure 1.a. In the cis isomer, the two B groups are adjacent to each other, while in the trans isomer, the two B groups are opposite each other.

Geometrical isomers are totally different compounds, having different physical properties, and often having different colors. In most synthesis, both isomers are obtained. Separation can be a problem, but because of the (usually) different solubilities and reactivities of the isomers, separation is possible. The first geometrical isomers were also identified by Werner, who in 1893 determined the structure of the inorganic geometric isomer pair cis- and trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

Geometrical isomers frequently contain bidentate ligands, which occupy two coordination sites. Ethylenediamine ($\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) is such a bidentate ligand. The two geometrical isomers of the compound to be synthesized in this experiment, dichlorobis(ethylenediamine)cobalt(III) chloride, $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$, are shown in Figure 1.b. This pair was also first investigated by Werner.

Numerous complexes of cobalt(III) are known and nearly have octahedral structures.

unstable because it is a powerful oxidizing agent and is reduced by water to $\text{Co}(\text{H}_2\text{O})_6^{2+}$.



However, the +3 oxidation state can be stabilized by replacing the coordinated water molecules with groups such as NH_3 , NO^- , CN^- , and $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$. Once Co^{3+} has coordinated with ethylenediamine and chloride ligands, it shows little or no tendency to oxidize water.

Experimental Procedure:

1. Heat about 300 mL of water in a 600-mL beaker and maintain at a moderate boil.
2. In an evaporating dish, combine 4.0 g of cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) with 10 mL of distilled water. To this, add 15 mL of 10% ethylenediamine (en). Place the evaporating dish on top of the beaker of boiling water. Stir the mixture over this steam bath for 40 minutes; maintain the volume of the solution at about 20 mL by occasionally adding small portions of water. During this process, the cobalt(II) is oxidized to cobalt(III) by the oxygen in the air. Good agitation is necessary to promote dissolution of the oxygen.
3. Transfer the apparatus to the fume hood and add 12 mL of concentrated 12M HCl. (*Note: HCl is corrosive - handle with extreme care.*) Continue the heating (in the hood) and stirring (without the addition of water) until a thin slurry of crystals has formed. Cool the slurry to room temperature by setting the evaporating dish on the lab bench. Stir occasionally for at least 15 minutes.
4. Filter the mixture using the filtering apparatus (250-mL side-arm flask, tubing, Buchner funnel) set up on the lab bench.

When the draining from the Büchner funnel has essentially stopped, add 5 mL of 6M HCl to the funnel and gently stir up the mixture with a spatula, taking care not to tear the filter paper. If the product is still brown or blue, repeat the washing process with 6M HCl. If the product is pure green, skip the washing to avoid loss of product.

5. Transfer the moist crystals of *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ to a clean watch glass. If there is enough time, dry the material on the steam bath. During the last stages of drying, powder the material on the watch glass by scraping and pressing with a spatula.

6. Transfer the dried product, *trans*-[Co(en)₂Cl₂]Cl, to a previously weighed scintillation vial (provided by your instructor). Reweigh and calculate the yield. At least 1.0 g of product should be obtained. Store your product.

Experiment 6. SYNTHESIS of cis-Dichlorobis(ethylenediamine)cobalt (III) Chloride

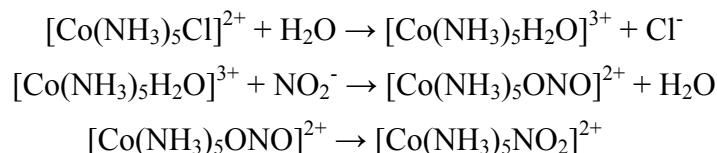
Experimental Procedure:

Place 0.2 g of the green trans-dichlorobis (ethylenediamine) cobalt (III) chloride on a watch glass. Dissolve this solid material in 6 ml of water and allow the solution to stand for about 10 min at room temperature. Place the watch glass on a water bath prepared from a 10 ml beaker containing a magnetic bar filled with boiling water. The beaker is previously positioned in a sand bath on a magnetic stirring hot plate. Heat the green solution and concentrate it to dryness. A deep violet, glassy material is formed on the watch glass.

Experiment 7. SYNTHESIS of nitritopentaamminecobalt (III) Chloride

Introduction:

The equations for the preparation of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ can be written as follows:



Experimental Procedure:

Start to heat a solution of 6.4 mL of coned, aqueous ammonia in 64 mL of water on the stirrer-hot plate. The surface temperature of the hot plate is not critical. While heating and stirring this solution, add 4 g of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (if 4 g of the chloropentaamminecobalt (III) chloride was not obtained in the previous experiment, adjust the reactants to the amount you obtained.) Continue heating and stirring until the colored product dissolves. If a dark brown to black precipitate of cobalt oxide forms, filter it off. Cool the filtrate which should be a clear solution to about 10 °C. Add 2M HCl slowly while keeping the solution cold until it is just neutral to litmus. Add 4 g of sodium nitrite followed by 4 mL of 6M HCl. After the solution has been in an ice bath for an hour, filter the precipitated salmon pink crystals of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ using a Buchner funnel. Wash with 20 mL of ice water, wash with 20 mL of alcohol, and then allow it to dry on the lab bench for one hour. The product is not stable and will slowly isomerize to the nitro compound.

Experiment 8. SYNTHESIS of nitropentaamminecobalt (III) Chloride

Experimental Procedure:

The nitritopentaamminecobalt (III) chloride in the previous experiment is isomerized to the nitro compound by heating. The nitrito compound prepared before can be utilized before it is dried. Bring 20 mL of water to a boil, add a few drops of aqueous ammonia, and add 2.0 g of the $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$. As this solution cools, add 20 mL of conc. HCl. After cooling the solution, the $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ will crystallize from the solution. Filter the product in a Buchner funnel, wash the product with 13 mL of alcohol, and allow it to dry in air for two hours.

Experiment 9. IR measurements

INFRARED SPECTROSCOPY

Introduction

Infrared (IR) spectroscopy is the most frequently used instrumental technique in organic laboratory courses, and is extensively used in inorganic chemistry as well. The most common type of IR spectrometer is the double-beam dispersive instrument (although the FTIR spectrometer is rapidly gaining in popularity). A diagram of a typical IR spectrometer is shown in Figure 1.

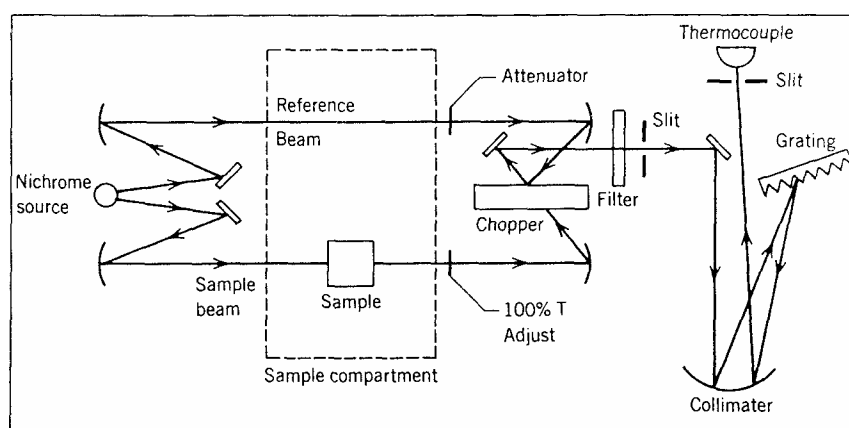


Figure 1. Schematic of a double-beam IR spectrometer

A hot wire serves as the source of IR radiation, which is divided into two beams: a sample beam and a reference beam. The sample beam is reflected by mirrors so that it passes through the sample cell, while the reference beam bypasses the sample. The beams are recombined at the chopper, pass through a filter, and passed through the monochromator entrance slit. The function of the chopper is to alternately pass the sample beam or reflect the reference beam to the slit. The beam then enters the monochromator, where the various frequencies are reflected by the collimator. This renders the beam rays parallel, and they then strike the reflection grating and are dispersed by refraction. For one angle of the grating, a specific frequency of radiation is diffracted back to the collimator. As the grating angle changes, different frequencies are swept. The beam is then reflected to a thermocouple detector. If no sample is in the beam, the temperature of the thermocouple will remain constant. If a sample is present, it will absorb some of the energy at various frequencies. The energy detected at the thermocouple will therefore rise and fall. The IR spectrum is a plot of

the transmitted energy (transmittance) versus frequency. The fact that there are two beams allows any substance present in equal quantities in both beams to "automatically cancel." Background materials, such as water vapor or CO₂ are thereby subtracted from the spectrum, instead of providing problems by absorbing in areas of interest.

Sample Handling

In order to obtain an IR spectrum, the sample must be placed in a holder that does not itself absorb in the IR region. This presents somewhat of a problem, as glass or quartz absorb in the IR, rendering them unsuitable for use. Instead, cells (also called windows or plates) made from fused salts (alkali halides or silver halides) are used.

For liquids of lower volatility (bp > 100 °C) the most common type of organic sample, one or two drops of sample are placed on one salt plate, and a second salt plate is placed over the first. The two are rotated relative to each other to "smear out" the sample. The two plates are placed in a cell holder, which is in turn placed in the spectrometer. A typical sample cell is shown in Figure 2. For more volatile liquids, a sealed cell (Fig. 3) or a gas cell (Fig. 4) must be used. One obvious difficulty comes in cleaning the cells after use. Obviously, water cannot be used, or else the cell will dissolve! Instead, dry acetone is usually employed to clean cells. Very dirty NaCl cells may be cleaned by rubbing them gently on a nonfibrous cloth onto which a few drops of Braso (a brass cleaner) were placed, followed by washing with absolute ethanol.

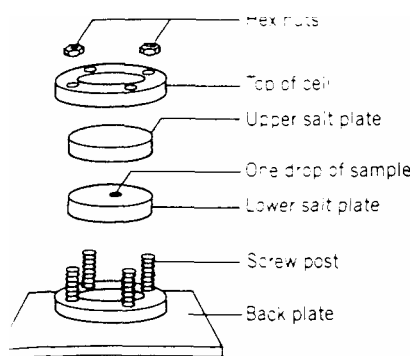


Figure 2. Infrared liquid cell

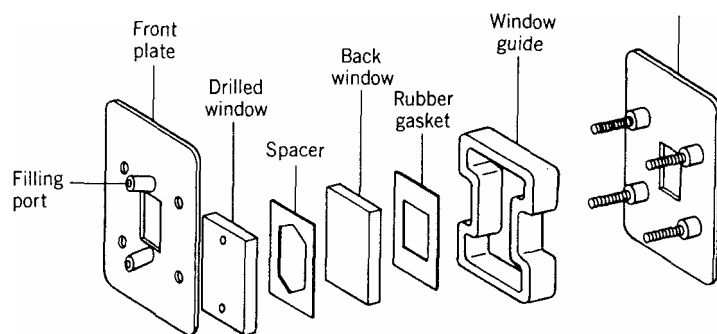


Figure 3. Infrared sealed-liquid cell

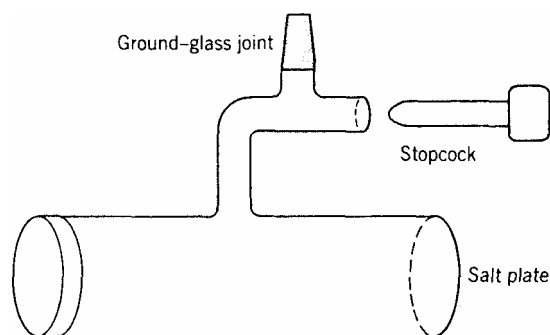


Figure 4. Infrared gas cell.

Gases (or volatile liquids) are handled by considering a small amount of into the nipple of a gas cell. The gas cell consists of two salt plates connected by a Pyrex tube with a path length appropriate to the spectrometer (~10 cm is normal.) The tube has a stopcock fused to it for attachment to a vacuum line. A gas pressure of about 10 mm is optimal for a good IR spectrum. The cell is shown in Figure 4.

Solids may be handled in several ways. The most common way is to dissolve or mull them in some liquid material that will not interfere in the IR region of interest. The material usually used as mulling agent is a mineral oil, Nujol. Nujol has absorbances in the IR region corresponding to C–H bonds. If the compound of interest has alkyl groups in its structure, Nujol will not be a good choice.

An alternative (and often better) method is to prepare a potassium bromide (KBr) disk. Approximately 5 mg of sample are finely ground in a mortar and 150 mg of finely ground KBr are added. The two materials are quickly mixed (there is some difficulty because of the hygroscopic nature of KBr) and placed in a pellet press cell. At high pressure, the KBr will

flow and seal the sample in a window of salt. Since KBr is transparent to IR radiation, IR spectrometer will detect only the sample. The cell should be disassembled and cleaned immediately after use, or else the corrosive nature of KBr to steel will result in damage to the cell.

Bond Vibrations.

The energy emitted in the IR region is sufficient to change the vibrational state in the bonds of molecules. In order for molecules to absorb IR radiation to induce bond vibrations, there must be a change in the dipole moment of the molecule as it vibrates. This change can be either in the size of the dipole moment or in its location. Consider the molecule HF. There is a dipole in this molecule, as fluorine is more electronegative than hydrogen. The dipole moment changes as the fluorine moves away from (or toward) the hydrogen as the bond stretches. On the other hand, a homonuclear diatomic molecule (such as N₂ or O₂) does not change in its dipole as it stretches. Therefore, N₂ and O₂ do not absorb in the IR region. (This is quite convenient; as otherwise, air would interfere with the desired IR signal of the sample we wish to investigate.) Infrared vibrations are strongest when the motion involves a large change in the dipole moment of the molecule. It is for this reason that unsymmetrical C – C single bond stretches are weak, and that C – O stretches are strong.

The frequency of the stretching vibrations are easily obtained using Hooke's Law,

$$\nu = \frac{1}{(2\pi c)} \sqrt{\frac{k}{\mu}}$$

where ν is the frequency of the vibration (in cm⁻¹), μ is the reduced mass of the atoms (in g) in the bond, c is the speed of light (2.998x10¹⁰ cm.s⁻¹), and k is the force constant for the bond (in dyne.cm⁻¹). The reduced mass is obtained via the equation

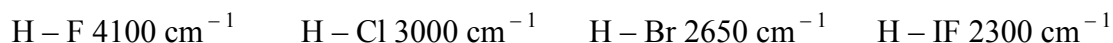
$$\mu = m_1 . m_2 / (m_1 + m_2)$$

where m_1 and m_2 are the individual masses of the atoms in the bond.

The size of the force constant, k , can be successfully related to the bond dissociation energy or the bond strength, if the molecules being compared are not too dissimilar. Thus, a strong bond is usually an indication of a large force constant. A plot of dissociation energy (or bond strength) versus force constant for a homologous series (e.g., HF, HCl, HBr, and HI)

generally results in a straight line.

From Hooke's law, it is easily seen that as the masses of the atoms (m_1 and m_2) increase, the reduced mass also increases and the vibrational frequency decreases. This "heaviness" trend is a general one, seen throughout the periodic table. For example, as the mass increases down the halogen family (neglecting changes in the force constants), the stretching frequency of the hydrogen halides decreases.



This trend might well be summarized as being a vertical trend in table.

The stretching frequencies for most common functional groups have been tabulated and need not be calculated. Bonds to hydrogen are generally seen at frequencies of 2000-4000 cm^{-1} . Bonds between moderately heavy elements appear somewhat lower, from 900 – 2700 cm^{-1} . (e.g., S – O, C – N, C – O, and N—O bonds). Bonds to heavier elements (e.g., C – Cl, Se – O, and P – Br) appear at low a vibrational frequency that is below 900 cm^{-1} . These stretching frequencies are tabulated in Figure 5.

Bonds to Hydrogen	Moderate Mass Bonds	Bonds to Heavy Elements
C—H 2900 cm^{-1}	B—F 1400 cm^{-1}	C—Cl 750 cm^{-1}
Si—H 2150 cm^{-1}	C—N 1100 cm^{-1}	C—Br 650 cm^{-1}
Ge—H 2100 cm^{-1}	C—O 1100 cm^{-1}	N—Br 690 cm^{-1}
N—H 3400 cm^{-1}	N—F 1070 cm^{-1}	O—Cl 780 cm^{-1}
P—H 2300 cm^{-1}	C=C 1650 cm^{-1}	O—Br 710 cm^{-1}
O—H 3500 cm^{-1}	C=O 1700 cm^{-1}	B—Cl 950 cm^{-1}
S—H 2600 cm^{-1}	C=C 2100 cm^{-1}	B—Br 800 cm^{-1}
F—H 4100 cm^{-1}	C=O 2170 cm^{-1}	S—Cl 520 cm^{-1}
Br—H 2650 cm^{-1}		P—Cl 515 cm^{-1}
I—H 2300 cm^{-1}		P—Br 390 cm^{-1}

4000 cm^{-1} 400 cm^{-1}

Figure 5 Infrared correlation chart.

Care must be exercised here, however, to distinguish between single, double, and triple bonds, as the frequency increases with bond order. This is due to the k term in Hooke's law. The first constant increases with the bond order. Thus, k is larger for triple bonds than for double bonds than for single bonds. Since k is in the numerator of Hooke's law, the frequency

increases with increasing k . For this reason, CN triple bond appears at higher frequency (2150 cm^{-1}) than a CN double bond (1650 cm^{-1}) and a CN single bond (1100 cm^{-1}).

A second factor affecting the force constant is the electronegativity difference between the atoms making up a bond. As the electronegativity difference grows larger, the bond strength increases. The force constant is related to the bond strength (so it increases) and the frequency of the vibration consequently increases. Thus, in the approximately equal mass bonds below, electronegativity; difference is the overriding criterion.



This trend might well be described as a horizontal trend, as electronegativity. increases across the periodic table. These trends are all correlated in “IR region” diagram, shown in Figure 6.

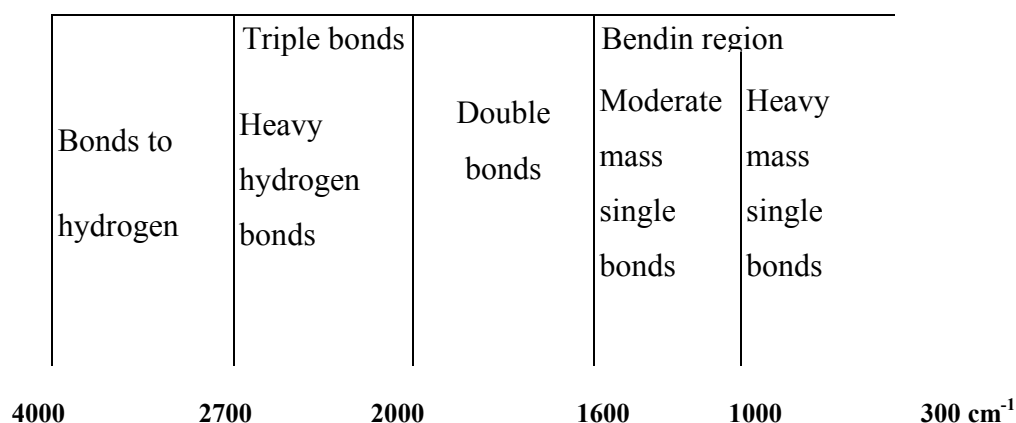


Figure 6 Infrared region diagram.

The motions involved in the common vibrational modes are shown in Figure 7. A plus sign indicates motion toward the reader, a minus sign away from the reader. In addition to the stretching vibrations discussed earlier, there are also signals associated with bending motions of bonds. Bending motions generally have much lower frequencies than stretching motions. For example the bending vibration associated with a C—H bond occurs between 1100 and 1500 cm^{-1} , compared to the stretching frequency of $2900\text{--}3100\text{ cm}^{-1}$. Some bending motions because a drastic change in the dipole of the molecule, and give rise to strong IR peaks. The most familiar cases occur in olefins, with very strong peaks appearing between 650 and 1000 cm^{-1} , depending on the type of the substitution. These correspond to the out of plane C—H bends. In acetylenes, there are strong absorptions between 610 and 700 cm^{-1} for the C—H

bends (If a CH bond is present). A useful region for aromatic compounds is between 650 and 850 cm^{-1} . This region corresponds to the bending motions of the aromatic hydrogen atoms of benzene. Monosubstituted benzenes exhibit two characteristic peaks between 690 and 710 cm^{-1} and between 730 and 770 cm^{-1} . Ortho disubstituted benzenes show a single peak between 735 and 770 cm^{-1} . Meta disubstituted benzenes show two peaks between 680 and 725 cm^{-1} and between 750 and 810 cm^{-1} . Finally, para disubstituted benzenes show a single peak between 810 and 850 cm^{-1} . These frequencies are useful in identifying phenyl substituted organometallic compounds. Other bending frequencies are shown in Figure 8.

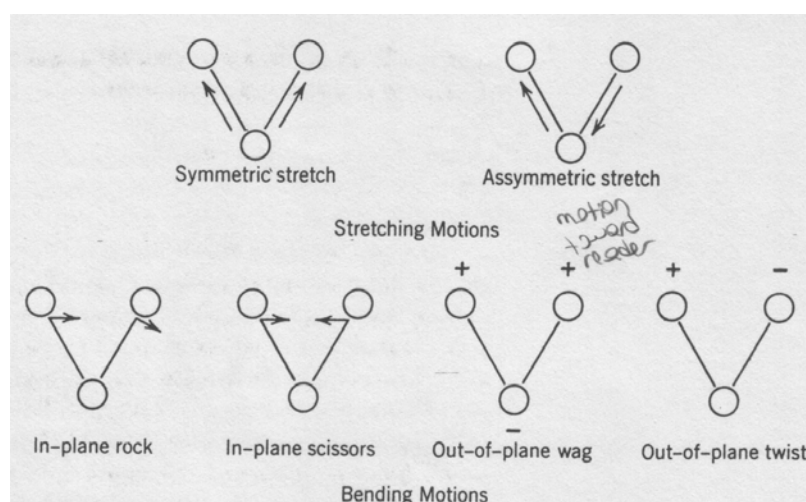


Figure 7. Vibrational modes

B—O	600–650 cm^{-1}
C—H (methyl)	1375 and 1450 cm^{-1}
C—H (methylene)	720 and 1465 cm^{-1}
C—H (olefin)	650–1000 cm^{-1} (very strong)
C—H (alkyne)	610–700 (broad)
C—H (aromatic)	See text
N—H	1590–1655 cm^{-1} (strong)
O—H	1330–1420 cm^{-1} (920 for acids, broad)
S—O	500–600 cm^{-1}
P—O	500–600 cm^{-1}
Se—O	400–450 cm^{-1}

Figure 8. Infared bending frequencies.

For molecules that are more complicated than diatomic, all atoms in the molecule undergo vibration in a synchronous manner. When a vibration involves the motion of a light group (e.g., C—H) in an otherwise heavy molecule (e.g., CHCl_3), very little motion of the heavier atoms occurs. The CH and CCl vibrations do not interact, and can be accurately predicted individually. If the vibration involves the motion of a group of the same mass as

other groups in the molecule, the vibrations can interact, and the whole molecule will be involved in the vibration. This leads to some variation in the position of a given band. For example C=O bands occur between 1600 and 1800 cm^{-1} , depending on the nature of the remainder of the molecule.

Apart from the frequency of the peak, the IR spectrum holds a wealth of other information. The shape of the peak, for example, is instructive. Broad bands indicate intermolecular interactions. Gas-phase spectra are usually much sharper than liquid-phase spectra, and in fact show fine structure associated with rotational motion. In liquids, this motion is damped out because of molecular interactions and collisions. Very broad bands in IR spectra are usually indicative of hydrogen bonding, and therefore usually correspond to OH and NH groups. In solid samples, the bands are usually even broader than in liquid samples. Infrared spectra of inorganic samples, which are usually solids, are therefore often of low resolution. Sharp bands in liquid or solid spectra usually indicate ring systems, most often aromatic ring systems.

Vibrational Modes

Geometry plays a large role in the interpretation of IR spectra, especially in inorganic chemistry. The number of fundamental vibrations in a spectrum is determined by the number of atoms and the geometry of the molecule. Imagine making a three-dimensional graph of any molecule. To graph any of the atoms, three coordinates must be specified (such as the x , y , and z coordinates in Cartesian space). For N atoms in a molecule, there would be $3N$ coordinates needed, or a maximum of $3N$ degrees of freedom. A degree of freedom corresponds to a molecular vibration, which will be IR active provided that a change in the dipole moment occurs.

Three of these $3N$ degrees of freedom correspond to moving the molecule in the x , y , and z direction without changing any of the bond lengths or angles. For a nonlinear molecule, three more of these $3N$ degrees of freedom correspond to rotating the molecule on one of the Cartesian axes, which also does not change any of the bond lengths or angles. For linear molecules, there two degrees of freedom corresponding to rotating the molecule. Since a bond length or angle must change in a molecule if an IR vibration takes place, these must be subtracted from the $3N$ degrees of freedom. Therefore, a linear molecule will have $3N - 5$ vibrations, and a nonlinear molecule will have $3N - 6$ vibrations.

There can be more bands observed in the IR spectrum than the $3N - 5$ or $3N - 6$ fundamental vibrations. The nonlinear molecule SO_2 would be expected to have three fundamental vibrations ($3 \times 3 - 6 = 3$). When the spectrum of the molecule is obtained (Fig. 9), seven signals are seen: 519, 606, 1151, (vs = very strong), 1361 (vs = very strong), 1871 (vw = very weak, sometimes not observed), 2305 (w = weak), and 2499 (s = strong) cm^{-1} .

Three of these frequencies (519, 1151, and 1361 cm^{-1}) indeed correspond to the three fundamental vibrations, and are called fundamental bands. The others correspond to combinations of the fundamental bands and are therefore termed combination bands. These combinations can occur as the sum of two fundamentals, as the difference of two fundamentals, or as a multiple of a strong fundamental. The band at 606 cm^{-1} is a difference band, corresponding to the difference between the 1151 and the 519- cm^{-1} fundamental bands. Note that the band (not shown in spectrum) does not occur at the exact difference, but near it. Similarly, the band at 1871 cm^{-1} is a sum band, corresponding to the sum of the 519- and 1361- cm^{-1} fundamental bands. The band at 2499 cm^{-1} is another sum band, corresponding to the sum of the 1151- and 1361- cm^{-1} fundamental bands. Finally, the band at 2305 cm^{-1} is an overtone band corresponding to double the frequency of the strong fundamental band at 1151 cm^{-1} .

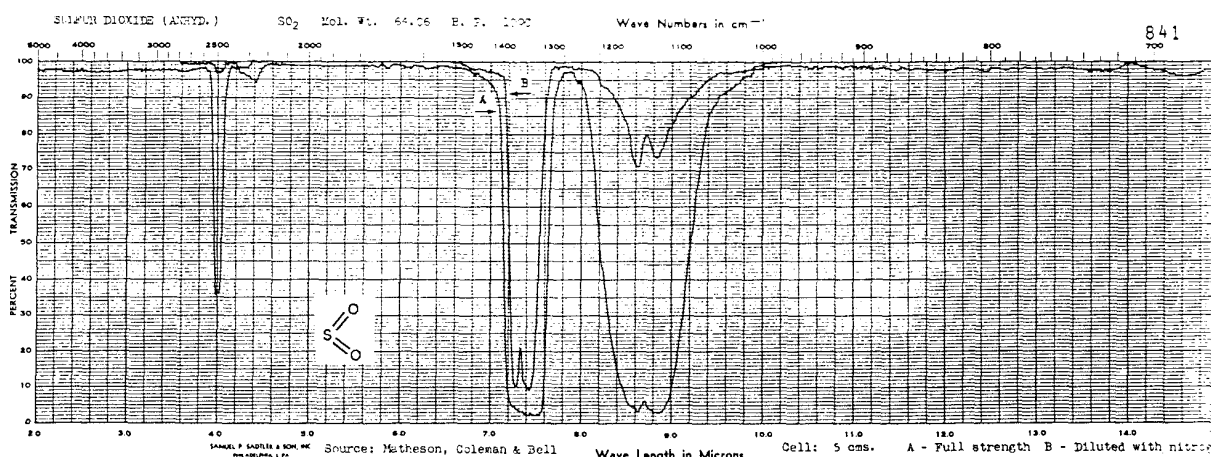


Figure 9. Infrared spectrum of sulfur dioxide. (© Sadtler Research Laboratories, Division of Bio-Rad

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With simple molecules, the fundamental and overtone bands are fairly straightforward to assign, but with more complex molecules, this becomes far more difficult. Further complications set in because not all of the predicted bands are active in the IR spectrum. In

some cases, no change in the bond-dipole moment occurs for a given vibration. The vibration, therefore, will not be IR active. In order to see some IR inactive vibrational frequencies, a second type of vibrational spectroscopy must be resorted to, called Raman spectroscopy. For a vibration to be active in the Raman spectrum, there must be a change in polarizability during the vibration. In most cases, a vibration that is not IR active will be Raman active, and vice versa. Some vibrations are active in both types of spectroscopy. A very small number of vibrations are active in neither type. For this reason, IR and Raman Spectroscopy are complementary techniques.

The geometry of a molecule (more specifically, its group symmetry) further determines the number of bands in the IR spectrum. In some cases, vibrations are degenerate, for example, more than one of the expected fundamental vibrations will occur at a given frequency. The number of fundamental absorptions in the IR spectrum therefore can be fewer (or greater—see above) than expected.

Inorganic Functional Groups

The horizontal and vertical trends discussed previously all apply to inorganic functional groups. One additional trend that must be considered deals with the charge on the central atom of the functional group. As a general rule, as the charge increases on the central atom, the atom becomes more electronegative, and the force constant consequently increases. Therefore, the frequency of absorption also increases.

The change in oxidation state is the most important factor in predicting the absorption frequency for an inorganic group, more important than small changes in the bond order. For example, the nitrite ion, NO_2^- , shows a strong band at approximately 1240 cm^{-1} , while the band for the nitrate ion, NO_3^- , occurs at approximately 1360 cm^{-1} . The N—O bond order in the nitrite ion is 1.5, whereas that in the nitrate ion is 1.33. On the basis of bond order, one would predict that the nitrite ion should occur at the higher frequency, but this is not the case. The oxidation state is the overriding criterion—the nitrogen in nitrite ion is in the III oxidation state, while that in the nitrate ion is in the V oxidation state. A similar trend is seen by comparing the frequencies of the chlorate, ClO_3^- and perchlorate, ClO_4^- , ions. Chlorate has a major absorbance at about 960 cm^{-1} , and as expected, perchlorate appears at a higher frequency, $\sim 1100\text{ cm}^{-1}$.

As seen earlier, the vertical trend is operative for inorganic groups. A further example can be seen in comparing the sulfate, SO_4^{2-} , ion with the selenate, SeO_4^{2-} ion. The sulfate shows

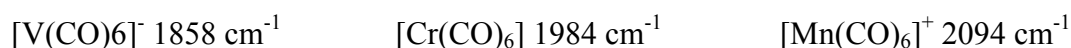
a strong S—O absorbance at 1110 cm^{-1} , and the selenate, which contains the heavier selenium atom, shows a strong Se—O band at about 830 cm^{-1} .

An important point to consider about the vertical trend is that it does not depend on the masses in the bond directly, but rather on the reduced mass. When two masses are substantially different, the reduced mass is essentially equal to the lighter of the two. Further increasing the mass of the heavy atom in the bond does not appreciably change the reduced mass. For example, the Cr—O band in the chromate ion, CrO_4^{2-} , occurs at about 875 cm^{-1} . Increasing the reduced mass in the Mo—O band in molybdate, MoO_4^{2-} , shows a small decrease in the IR frequency to about 825 cm^{-1} . Increasing the mass further in tungstat WO_4^{2-} shows that the frequency for the W—O band has not appreciably changed, ranging from 820 to 830 cm^{-1} .

Synergistic Effects

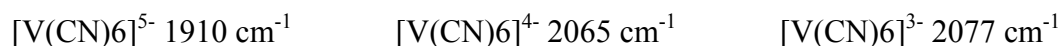
When transition metals interact with ligands that possess π electrons, there are two modes of bonding in evidence. The ligand donates electrons to the empty metal d orbitals (the $d_{x^2-y^2}$ and d_z^2 orbitals), while the metal "back-donates" electrons from its π orbitals (d_{xy} , d_{yz} , and d_{xz}) to the empty ligand π antibonding orbitals. This type of bonding is termed synergistic bonding.

One ligand that was extensively studied in this regard is the carbonyl ligand CO. In the free state, as carbon monoxide gas, the CO triple bond stretch occurs at 2143 cm^{-1} , while the CO double bond stretch in a ketone occurs at about 1700 cm^{-1} . In metal carbonyls, the metal would donate electrons to the π antibonding orbital of the carbonyl ligand, thereby reducing the bond order from three (in the case of carbon monoxide) to somewhat less than three. The degree of decrease in the bond order, and consequently in the stretching frequency, depends on the ability of the metal to donate electrons. Clearly, the more positively charged the metal ion, the less likely it is to donate electrons. This trend is seen in the following series:



Vanadium, with the lowest oxidation state (—I) is the best electron donor, and the frequency of the carbonyl band is the lowest. Manganese, having the highest oxidation state (I) is the poorest donor, resulting in a carbonyl frequency not far from carbon monoxide itself. Chromium (oxidation state 0) is intermediate.

This trend may be contrasted with metal cyanide complexes. The cyanide ion is a better σ donor, but a much poorer π acceptor than the carbonyl. This is due to the negative charge on the cyanide ion, which lowers the ion's ability to accept additional electron density donated by the metal. The ability of the metal to donate electrons is therefore not relevant in this case. However the ability of the metal to accept electrons in σ orbitals is of paramount importance. The higher the charge on the metal, the more able it is to accept σ electrons. This is seen in the trend



As the vanadium ion becomes more positively charged (from the I oxidation state to III), the frequency of the cyanide group increases, the opposite trend from that observed with the carbonyls.

In summary, the IR spectrum gives valuable information as to the nature of bonding and oxidation state in a compound or complex. These cases are also illustrated and discussed within specific laboratory experiments.

Interpretation of IR Spectra

The fundamental question to be asked is "Given an IR spectrum, how do I decide what the compound is?" Suppose you are preparing a new compound, and want to know if the preparation was successful. If you were trying to add chlorine to a boron compound, you might look at the 950-cm^{-1} region of the product and of the starting material. If your starting material did not have a peak in that area, and your product does, then you have almost certainly been successful, as B—Cl vibrations occur at approximately 950 cm^{-1} . In this case, you might conclude that the preparation was successful. In the absence of such a peak, the likelihood is that none of the desired product was obtained. Of course if the starting material had a peak in that area, it might be difficult to determine if the desired product was obtained.

Often, the compound of interest has been prepared before by others and its IR spectrum has been published. Good sources for published spectra are the Aldrich Library of FT IR Spectra (Aldrich Chemical Company) and the Sadtler IR Spectra compendia (Sadtler). In the case of a published spectrum, all one need do is compare the experimental spectrum of the product to the published spectrum of the desired product. If they match, the preparation was obviously successful.

The most difficult case occurs when you have no idea what the product might be, and wish to characterize it using IR Spectroscopy. In this case, there is a useful sequence of attack.

Step 1 Look at the overall spectral band shapes. An ultra sharp spectrum indicates an aromatic compound. Broad resonances indicate inorganic groups. Very broad resonances indicate hydrogen-bonding groups.

Step 2 Check the region between 1600 and 2800 cm^{-1} . Any peak in this region is of interest and gives helpful information about the compound. For example, a peak at 1700 cm^{-1} indicates a C=O bond, and a peak at 2050 cm^{-1} indicates a C≡N triple bond in a cyanide or thiocyanide group.

Step 3 Investigate the region above 3000 cm^{-1} . Hydroxyl groups give broad and obvious bands at 3500 cm^{-1} . Amines give strong peaks at 3300 cm^{-1} . Terminal alkynes give a sharp (but weak) band at 3200 cm^{-1} . Alkenes give moderate bands at 3100 cm^{-1} .

Step 4 If the compound has aromatic functionalities, check the bending region at 650-850 cm^{-1} .

Step 5 Recognize that neutral unsaturated groups bonded to metals tend to absorb at somewhat lower frequencies than in the free compound. For example, the CO triple bond normally appears at 2100 cm^{-1} . In metal carbonyls, however, the frequency is lowered substantially because of the donation of electrons from the metal to the carbonyl antibonding orbitals. In fact, the frequency of the carbonyl stretch is a sensitive indication of the oxidation state of the metal.

Step 6 Once you have determined what type of compound you have using Steps 1—5, look up the spectra of likely possibilities, and compare your experimental spectrum to the published ones.

A more recent innovation is the computer spectral search program. One inputs to the program the IR peak wavenumbers, and the program searches its files, and tells the user which compounds are likely matches. Many advanced instruments have such search programs built in, and several "stand alone" programs are available that operate using a personal computer. These programs are geared mainly for organic chemicals, but in many cases include substantial

numbers of inorganic and organometallic compounds as well. Programs are available from Aldrich Chemical Company (for organic compounds), from Sigma Chemical Company (mainly biochemicals), and from Sadtler.

Fourier Transform Infrared (FTIR)

Traditionally, most laboratories were equipped with dispersive IR spectrometers of the type discussed earlier. Recently, with the falling prices associated with microcomputers, the FT IR spectrometer has increased in popularity, taking a larger and larger share of the market. The cost of an FT IR spectrometer can be as low as \$16,000, with \$25,000 being the average price of a fully functional entry level instrument. The FT IR spectrometer offers several important advantages over the dispersive instrument. These advantages arise from two factors: an FT IR uses an interferometer instead of a monochromator, and the output data from an FT IR is stored in digital form in a computer memory, and can be manipulated.

The interferometer consists of one fixed and one movable mirror, and a beamsplitter. A source provides radiation, much like a dispersive spectrometer. One half of the radiation is reflected by the beamsplitter, strikes the fixed mirror, and is reflected back to the detector. The other one half of the radiation is transmitted by the beamsplitter to the movable mirror and is reflected back to the detector. The distance from the beamsplitter to the fixed mirror is constant, while the distance from the beamsplitter to the movable mirror is variable both distances are equal, the two beams of radiation interfere constructively. If the distances are different by $\lambda/2$, where λ is the wavelength of the radiation: the beams interfere destructively. The intensity of the beam at the detector therefore depends on the position of the movable mirror, and follows the equation

$$I(x) = B(\nu) \cos(2\pi x\nu)$$

where $I(x)$ is the intensity of the signal, and $B(\nu)$ is the intensity of the source radiation at frequency ν . The difference between the mirror distances is as x . This mirror arrangement is shown in Figure 18. The source in an FTIR spectrometer is polychromatic, however, and there will be a cosine wave each of the frequencies. The intensity equation therefore depends on the sum of all the individual cosine waves.

$$I(x) = B(\nu_1) \cos(2\pi x\nu_1) + B(\nu_2) \cos(2\pi x\nu_2) + \dots$$

or

$$I(x) = \int B(\nu) \cos(2\pi x\nu) d\nu$$

This equation is essentially constant for all values of x , except when the two mirror distances are equal ($x = 0$) and the beams interfere constructively. At this point, there will be a "burst" at the center of the interferogram. If a compound is placed in the source path, it absorbs certain frequencies from the polychromatic source. This subtracts cosine waves from the interferogram pattern. The difference between the two interferograms (source only and sample + source) must be due to the sample itself. By performing a Fourier transform (a mathematical technique) on the interferogram, the "normal" spectrum is obtained.

The advantages of FTIR can be enormous. Since the data is stored on a computer, instead of taking one scan of the sample, multiple scans can be taken. (They can also be taken with dispersive instruments, but the price then rises to be roughly equal to that of an FTIR.)

The signal is always present in the interferogram, but the noise present is random, and will partially average out as \sqrt{N} , where N is the number of scans; The net gain in signal-to-noise (S/N) ratio is therefore $N/\sqrt{N} = \sqrt{N}$. For example if 100 scans are taken, the S/N ratio will increase by a factor of 10. This is known as Fellgett's advantage. A further advantage is that an interferometer has a circular entrance opening versus the entrance slit of a dispersive instrument.

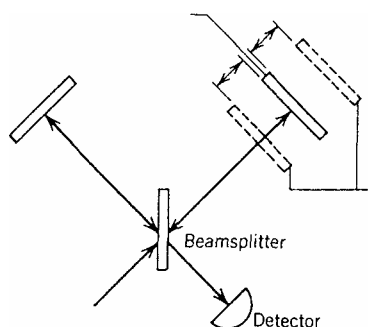


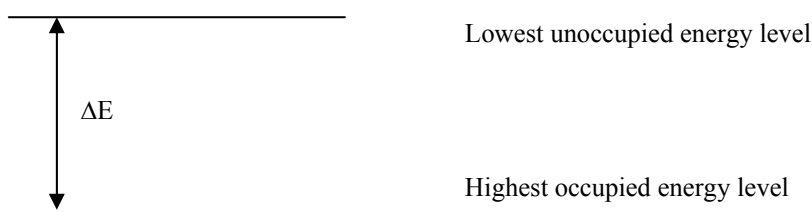
Figure 10. Fourier Transform infrared interferometer.

Experiment 10. $10D_q = \Delta_0$ measurements of hexaaqua complexes of 1st series transition metals.

Introduction:

Spectroscopy

In an atom, molecule, or ion, there energy levels corresponding to various physical changes that may be undergone by the particle. Generally, the lower energy state (or states) is occupied and the higher energy state (or states), is unoccupied. Suppose that the difference in energy between the highest occupied state and the lowest unoccupied state is ΔE . By irradiating the particle with energy corresponding to ΔE , a transition between these states may be induced.



The energy of the radiation is related to the frequency of the radiation via the equation:

$$\Delta E = h\nu$$

where h , is Planck's constant, 6.626×10^{-34} J.s, and ν is the frequency in Hertz.

Frequency is related to wavelength in the following way:

$$\nu = c / \lambda$$

where c , is the speed of light, 2.998×10^8 m.s⁻¹. Thus,

$$\Delta E = h\nu = hc / \lambda = hc\omega$$

where ω is the wave number, defined as the reciprocal of the wavelength.

The frequency range for the transition will depend on the energy difference. Some of the ranges are listed in Table 1.

Table 1: The ranges of electromagnetic spectrum.

Region	Wavelength (nm)	Energy	Change Excited
Gamma (γ) ray	$<10^{-10}$	$>10^6$ kJ mol ⁻¹	Nuclear Transformation
X-ray	10^{-8} - 10^{-10}	10^4 - 10^6 kJ mol ⁻¹	Inner-shell electron transitions
Ultraviolet (UV)	4×10^{-7} - 10^{-8}	10^3 - 10^4 kJ mol ⁻¹	Valence shell electrons
Visible	8×10^{-7} - 4×10^{-7}	10^2 - 10^3 kJ mol ⁻¹	Electronic Transitions
Infrared (IR)	10^{-4} - 2.5×10^{-6}	1-50 kJ mol ⁻¹	Bond Vibrations
Microwave	10^{-2} - 10^{-4}	10-100 kJ mol ⁻¹	Molecular Rotations
ESR	10^{-2}	10 kJ mol ⁻¹	Electron Spin Reversals
NMR	10	0.01 kJ mol ⁻¹	Nuclear Spin Reversals

Both IR and Visible spectroscopy are type of absorption spectroscopy. The major difference the two types is the frequencies at which they operate, the consequent energies involved.

The energy of an atom or molecule depends on which orbitals in the system are occupied by electrons. The separation of these electrons energy levels is large, on order of tens of kilojoules per mole. Visible spectroscopy operates at frequencies corresponding to the energy electronic transitions from the molecular ground state to excited states, usually from one *d* orbital to another in the case of transition metals.

Molecules have other kinds of energy as well. The bond length of a molecule is not constant. It undergoes vibration similar to the situation of two weights connected by a spring. Only certain vibrational energies are allowed. The separation of these vibrational levels is on

the order of a few kilojoules per mole. This gives rise to IR spectroscopy.

Spectrometer Components

There are several components that are common to most types of instruments used to obtain Visible or IR spectra. First, a source of radiant energy is necessary. In the case of IR spectroscopy, the source is usually a silicon carbide rod heated to approximately 1200 °C (called a Globar) or a zirconium oxide-yttrium oxide rod (called a Nernst glower) heated to 1500 °C or a nichrome wire. In the case of Visible spectroscopy, the source is a tungsten filament lamp. In these instruments the source emits continuous radiation over a fairly wide range of wave-lengths, In general, however, a narrower bandwidth is desired to obtain greater resolution and sensitivity.

The narrow bandwidth is achieved through the use of a monochromator. The polychromatic radiation emitted by the source is resolved into its individual wavelengths. In simplest terms, the monochromator consists of an entrance slit to allow the source radiation in, a collimating lens or mirror, a prism or grating, a focusing lens, and an exit slit. A simple prism monochromator is shown in Figure 1. All parts of the monochromator must be transparent in the spectral region of interest, so as not to interfere with the desired signal.

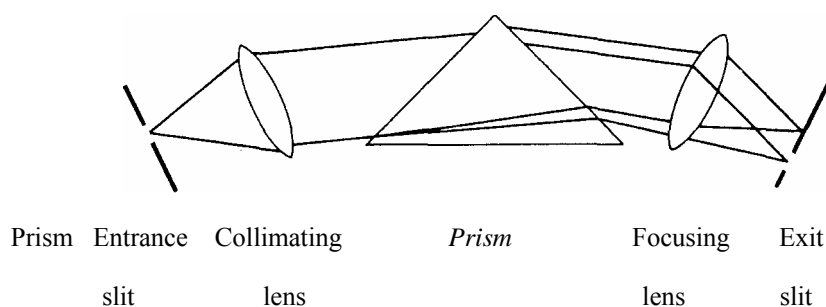


Figure 1: A prism monochromator.

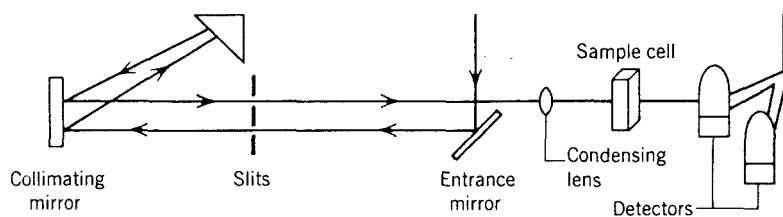


Figure 2. UV-Visible *single-beam spectrometer*

The radiation, which is now monochromatic, then strikes the absorption cell, and the material within it undergoes a transition to a different energy state. When the material relaxes back to the ground state, it releases energy, which is measured by a detecting device, and the resulting signal is then displayed by an oscilloscope or recorder. A schematic diagram of a single-beam Visible spectrophotometer is shown in Figure 2.

There are two basic types of instruments: single or double beam. In a double-beam instrument, a beam splitter splits the source radiation prior to the absorption cells. One beam goes to the sample and another goes to a blank or reference cell. The two beams are continuously compared and deviations in the source due to whatever cause can be compensated for automatically. Given the high stability of most sources, a double-beam instrument (which is more expensive) is not necessary for many purposes.

VISIBLE SPECTROSCOPY

Introduction and Theory:

The Visible spectrophotometer is the most commonly used instrument in academic laboratories and the third most commonly used in industry.¹ One of the more appealing aspects of inorganic chemistry (transition metal chemistry in particular) is that many compounds have absorptions in the Visible region, and therefore appear colored. The Visible range of the electromagnetic spectrum is depicted in Figure 3.

Visible absorptions usually involve electronic transitions between d or; electron energy levels, although charge-transfer bands also frequently occur in the Visible region. The simplest example of the d-d type of transition is for a species with a single d electron, such as $[\text{Ti}(\text{i-}i20)6]^{3+}$.

The d orbitals in octahedral complexes are divided into two energy groups, shown in Figure 4. Other geometries split the d orbitals in a different manner.

In a vacuum, the five d orbitals are all of equal energy—that is, they are said to be degenerate. This is only true, however, in the free ion. Thus, in Ti^{3+} , for example, the d orbitals

are all degenerate, but in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, they are not. The d_{xy} , d_{yz} , and d_{xz} orbitals have their lobes directed between the Cartesian axes, and the $d_{x^2-y^2}$ orbitals have their lobes directed on the Cartesian axes.

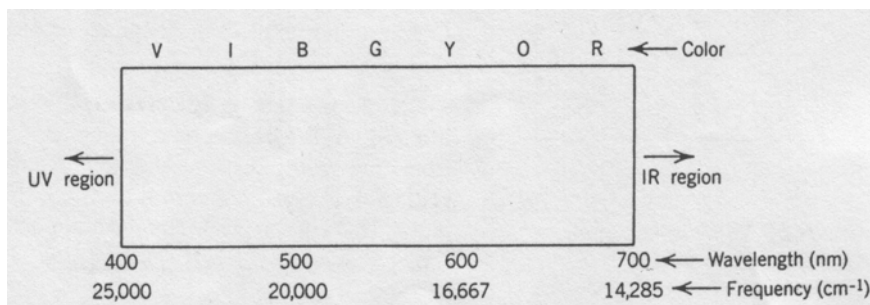


Figure 3. The Visible region of the electromagnetic spectrum

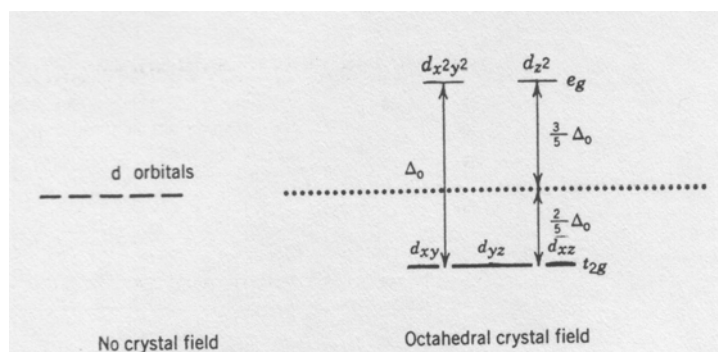


Figure 4. Octahedral crystal field splitting

In an octahedral molecule or ion of formula ML_6 , the metal can be viewed as being positively charged, and the ligands as being negatively charged. The structure of this arrangement is shown in Figure 5. The d orbitals contain electrons, and are thereby negatively charged. If any orbital lobe is directed at a negatively charged ligand, there will be a repulsion between them. This repulsion destabilizes these orbitals, which consequently rise in energy. The $d_{x^2-y^2}$ and d_{z^2} orbitals fall into this category. The d_{xy} , d_{yz} , and d_{xz} orbitals are not directed at the ligands, and there is little repulsion. These orbitals are therefore more stable than the $d_{x^2-y^2}$ and d_{z^2} orbitals. In fact, they are stabilized relative to the d orbitals of the free ion.

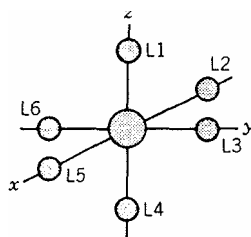


Figure 5. Orientation of ligands in an octahedral complex.

The d_{z^2} orbital lobes are pointed directly at ligands 1 and 4. The $d_{x^2-y^2}$ orbital lobes are pointed directly at ligands 2,3,5, and 6. It can be shown that the two orbitals are equally destabilized, and that the d_{xy} , d_{yz} , and d_{xz} orbitals are equally stabilized. The orbital energies are thereby split in the manner shown in Figure 4. Since the total energy of the five orbitals must be conserved, the relative stabilizations can be calculated. The t_{2g} orbitals must be stabilized (call this x) by the same amount that the e_g orbitals are destabilized (call this y). Thus,

$$3x = 2y$$

and since

$$x + y = \Delta_0$$

the two equations may be solved to obtain $x = 2/5 \Delta_0$ and $y = 3/5 \Delta_0$. The t_{2g} orbitals are therefore stabilized by $2/5$ the value of Δ_0 and the e_g orbitals are destabilized by $3/5$ the value of Δ_0 .

In the octahedral case, the lower energy level is known as the t_{2g} level, and the upper level is the e_g level. The energy difference between these levels is given the symbol Δ_0 , the o standing for octahedral. Since the titanium complex has only one electron, it will be found in the lower energy orbital, the t_{2g} level. Common terms used in designations of energy states are listed in Table 2.

Table 2 Energy State Terms.

a and b	Singly degenerate orbital
e	Doubly degenerate orbital
t	Triply degenerate orbital
g	<i>gerade</i> , phase of the orbital symmetric with respect to inversion
u	<i>ungerade</i> , phase of the orbital not symmetric with respect to inversion

The Visible Spectrum

If energy at the appropriate frequency (corresponding to energy A_0) is applied from the source of a Visible spectrophotometer, the single electron of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, will undergo a transition from the lower (t_{2g}) energy level to the higher (e_g) energy level. The Visible

spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is shown in Figure 6.

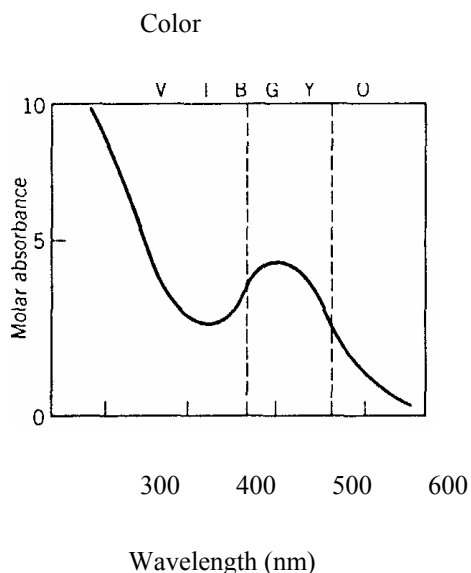


Figure 6 Visible Spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

The maximum absorbance occurs at about 510 nm. This is in the green-yellow region of the Visible spectrum. Keep in mind that this is the color absorbed. The color of a compound depends on the color transmitted, which is the complement of the absorbed color. Thus, the complex appears to be red-violet in color. Since the absorption wavelength depends on ΔE between the t_{2g} and e_g levels, Δ_0 for this complex can be calculated as follows:

$$\Delta_0 = h\nu = hc/\lambda$$

$$\Delta_0 = (6.626 \times 10^{-34} \text{ J}\cdot\text{s}) (2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}) / (510 \times 10^{-9} \text{ m})$$

$$\Delta_0 = 3.9 \times 10^{-19} \text{ J}\cdot\text{molecule}^{-1} = 230 \text{ kJ}\cdot\text{mol}^{-1}$$

This falls well within the range 100-1000 kJ found in Table 1 for Visible absorptions.

Molar Absorbance and Color

The strength of the molar absorbance in a given material depends on whether the quantum mechanical selection rules for electron transitions are obeyed. There are two selection rules that are of interest here.

1. If a molecule's geometry has a center of symmetry, transitions from one centrosymmetric

orbital to another are forbidden (symmetry forbidden rule).

2. If the number of unpaired electrons in a molecule changes upon electronic transition, the transition is forbidden (spin forbidden rule).

If neither selection rule is violated, the electronic transition is allowed. If one rule is violated, the transition is forbidden and if both rules are violated, the transition is doubly forbidden.

The octahedral geometry has a center of symmetry. Transitions between two d orbitals are therefore forbidden by the symmetry rule. The only reason that such transitions can be seen at all is that the vibrations undergone by the octahedron cause deviations from perfect centrosymmetry. Such singly forbidden transitions have weak molar absorbances, on the order of 1—10. The molar absorbance of the band in Figure 6 is ~5. The colors arising from such d—d transitions are of the "pastel" variety. Since tetrahedral geometry does not have a center of symmetry, tetrahedral d—d transitions are much stronger than octahedral ones, and give rise to deeper color.

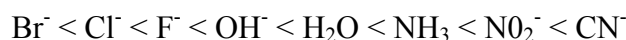
Allowed electronic transitions have intensities of 1000—100,000. The most common example of this type of transition is in the case of charge-transfer transitions. Here the electron moves from an orbital centered mainly on the metal atom to one on the ligand (or vice versa). The energy for this type of transition is usually higher than for a d-d transition and therefore occurs at higher frequency. When such transitions occur in the Visible region, they are usually at the extreme violet end, and give rise to extremely deep color.

Octahedral manganese(II) complexes provide examples of doubly forbidden d—d transitions. There are five unpaired electrons in the ground state for most manganese(II) complexes (all t_{2g} and e_g orbitals singly occupied). There is no way of rearranging the electrons in the d orbitals without pairing up at least two of them. The number of unpaired electrons must therefore change during a transition, and the d-d transition is therefore doubly forbidden. Doubly forbidden transitions give rise to very weak color, with manganese(II) being very pale pink. Tetrahedral manganese(II) complexes give rise to somewhat stronger color as the transitions are only spin forbidden, and are usually yellow-green.

Size of the Crystal Field Splitting

The size of the crystal field splitting, Δ_o , depends on several factors, which include the type of metal, the type of ligand, the charge on the metal, and the geometry of the complex. Several trends will be summarized here.

1. The size of Δ_o increases from the first to the third transition metal series. Second-row metals have Δ_o values 25-50% larger than first-row metals. Third-row metals show similar increases relative to second-row metals.
2. With certain ligands, the size of Δ_o is larger than with other ligands. The ordering of ligands in terms of the size of Δ_o induced is termed the **spectrochemical series**. The order of some of the more common ligands is



3. The size of Δ_o increases sharply with increasing charge on the central metal.
4. The geometry adopted by the complex has large effects on the crystal field splitting. In tetrahedral complexes, for example, the splitting, Δ_t , is only four ninths the size of the equivalent splitting in an octahedral complex.

Energy Level Diagrams

As discussed earlier, the situation for a d^1 ion is quite simple, with the only transition possible being from the t_{2g} to the e_g orbital. The energy diagram for such a d^1 system is shown in Figure 7. With more than one electron in the d orbitals, the situation becomes much more complicated, as there are many possible ways that the electrons can occupy the orbitals. Even in the seemingly simple case of two p electrons, there are no fewer than 15 possible arrangements for the two electrons! The energy diagram for a d^2 ion is shown in Figure 8.

Each line on the energy level diagram represents the energy of a particular electronic

arrangement of two d electrons within the five d orbitals. The lowest energy line [labeled ${}^3T_1(F)$, read as triplet T-one-F] is termed the ground state. The superscript three for this energy state is the multiplicity of the state, and obtained by the equation²

$$\text{multiplicity} = n + 1$$

where n is the number of unpaired electrons. All transitions normally seen in the Visible spectrum occur from the ground state to an excited state.

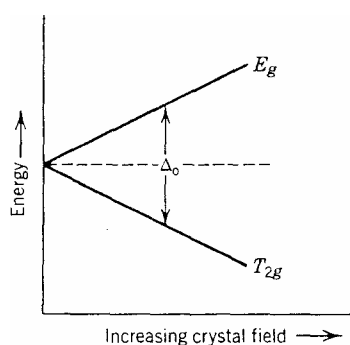


Figure 7. Energy level diagram for d^1 octahedral complex.

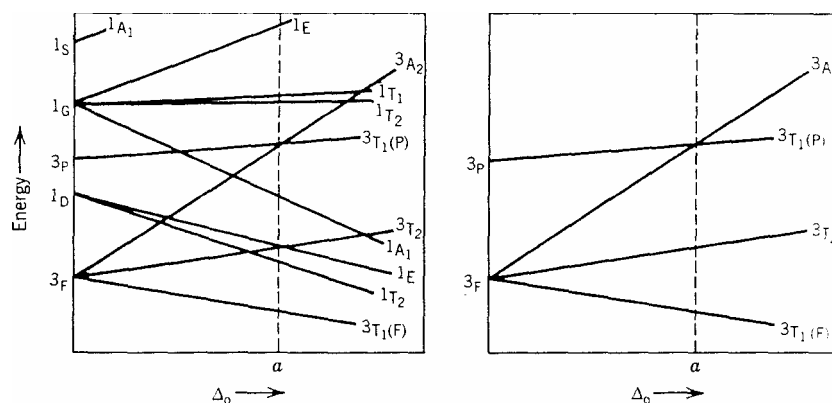


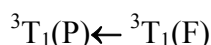
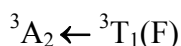
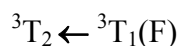
Figure 8. Energy level diagrams for d^2 octahedral complex.

Recalling the selection rules, transitions from the ground state to excited energy states are only allowed if the number of unpaired electrons does not change (e.g., the multiplicity remains constant). The energy levels for states of different multiplicity can usually be neglected, and the resulting energy level diagram simplifies considerably. The diagram on the left of Figure 8 shows all energy states, while the one on the right shows only the triplet states, to which transitions will not be spin forbidden.

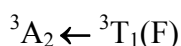
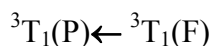
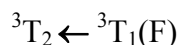
At room temperature, only the ground state, ${}^3T_1(F)$, is occupied. Since there are two

3T_1 , states, they must be distinguished from each other. The (F) notation refers to the 3T_1 , state that arose from the splitting of the original F state. When the spectrophotometer scans the complex at different frequencies, transitions are induced from the ground state to excited states. Since the ground state is a triplet, the main transitions will be to other triplet states.

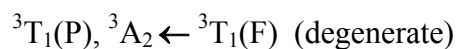
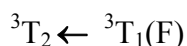
At values of Δo below a in Figure 8, the transitions would be



At values of $\Delta o > a$, the transitions would be



At $\Delta o = a$, only two transitions would be seen.



The frequency of an absorbance in the Visible spectrum may be used to calculate the energy difference between the ground state and an excited state. In this manner, we can determine "where in the energy diagram we are." Using the frequency of the transition ν , we can calculate ΔE . The energy level diagram is then searched for the location where a transition from the ground state to an excited state has the calculated value of ΔE . In practice, it can be even more difficult than this to assign the transitions, as the various energy levels can interact in different ways, leading to even more complicated energy diagrams and spectra.