Inorganic Chemistry (CH258) Spring 2001 Gustavus Adolphus College

PREPARATION AND ANALYSIS OF TRANSITION METAL NITRITE COMPLEXES

Introduction

Metal ions, being Lewis acids, tend to bond to chemical species that are electron-rich relative to each particular metal ion. The bonding in these metal complexes (also known as coordination compounds) covers a continuum from predominantly ionic to predominantly covalent, and is dependent on the nature of both the metal and the molecule or ion which is bound to the metal (such a bound species is called a ligand). Examples of complexes which are bound predominantly by ionic forces (ion-dipole interaction) are aqueous alkali metal ions (where the water molecules of solvation act as ligands), and crown ether complexes of alkali metal cations. Compounds such as ferrocene, $Fe(C_5H_5)_2$, and bis(benzene)chromium(I) cation, $(C_6H_6)_2Cr^+$, where the metal is bound to the hydrocarbon through the hydrocarbon's π system, exhibit predominately covalent bonding. The bonding in coordination complexes such as $Cu(NH_3)_4^{2+}$ and $Fe(CN)_6^{3-}$ falls between these two extremes.

Many ligands can be grouped according to the number of individual electron pairs which they are able to donate for coordination to a particular metal. Unidentate (literally `one-toothed') ligands donate one electron pair; bidentate ligands [also known as chelating ligands, from the Greek word chele (claw)] donate two electron pairs, tridentate ligands three, and so forth. Polydentate ligands generally form complexes which are more stable than those of the analogous unidentate ligands. This stabilization arises because the entropy of complexation is less unfavorable for the polydentate ligands, which are pre-arranged into structures which can easily attain the proper geometry for complexation. For example, the tris(ethylenediamine) complex[1] of Co(II) is much more stable than the hexakis(ammine) complex[2], even though they are similar in that both have six sp^3 nitrogen atoms bound to cobalt.

Stability of Coordination Complexes

The stability referred to in the preceding paragraph arises from the thermodynamics of the complexation reaction. A second type of stability arises from the rate at which the ligands can exchange for other ligands. A complex that is stable toward ligand interchange (i.e. exchange occurs very slowly or not at all) is called an inert complex; if ligand exchange occurs rapidly, the complex is termed labile. An inert complex is not necessarily stable in a thermodynamic sense - inertness arises simply from a high activation energy (lack of a suitable low-energy path) for substitution.

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[1] ethylenediamine is a common non-IUPAC name for 1,2-ethanediamine, $H_2N\text{-}CH_2CH_2\text{-}NH_2$

[2] $Co(NH_3)_6^{2+}$

Synthesis of Hexanitritometallate Complexes - Background

The ligand that will be used in this experiment is nitrite ion, NO_2^-. The transition metal ions Co^{2+}, Cu^{2+}, Ni^{2+} react with nitrite in aqueous solution to form complexes in which six nitrite ions have been bonded to the metal ion, as illustrated below for copper(II).

$$Cu^{2+}_{(aq)} + 6NO_2^- \longrightarrow Cu(NO_2)_6^{4-}$$

The hexanitritometallate(II) ions form salts of low solubility with a combination of potassium ion and alkaline earth cations. The preparation of these substances is illustrated by the general equation below. Only certain combinations of potassium ion, alkaline earth metal ion, and transition metal ion will yield an insoluble salt; the best combinations are listed in Table I. All of the compounds contain one alkaline earth ion and one transition metal per mole of compound.

$$6KNO_2 + M'Cl_2 + MCl_2 \longrightarrow 4KCl + K_2M'M(NO_2)_6$$

$$M' = \text{Ca, Sr, or Ba} \qquad M = \text{Co, Cu, or Ni}$$

TABLE 1. Best Combinations of Transition Metal and Alkaline Earth Metal Ions for Formation of Sparingly Soluble Polynitritometallate(II) Salts

Transition Metal Ion	Alkaline Earth Metal Ions
Ni^{2+}	Ca^{2+}, Sr^{2+}, or Ba^{2+}
Co^{2+}	Sr^{2+} or Ba^{2+}
Cu^{2+}	Sr^{2+}

Some of the combinations form hydrates. Spectral and chemical analysis of the complexes can be used to determine whether or not the compound is hydrated, and, if so, to what extent.

Chemical Analysis of Hexanitritometallate Complexes - Background

The hexanitritometallate complexes are all labile, so the nitrite ligand is easily removed if a suitable driving force for its detachment from the transition metal is provided. The amount of nitrite in a sample can be quantitatively determined by reaction with sulfamic acid (procedure described below); thus, analysis of a sample of an accurately known mass of hexanitritometallate complex should allow one to calculate the number of water molecules per mole of compound.

Nitrite ion is the conjugate base of nitrous acid, HNO_2 (molecular structure H-O-N=O). Nitrous acid is a weak acid, $pK_a = 3.29$, which means in turn that nitrite ion is a reasonably good weak base in aqueous solution. The basicity of nitrite, coupled with the lability of the nitritometallate complexes, allows nitrite to be removed from the transition metal and converted to nitrous acid simply by dissolution of the complex in a solution of strong acid.

Nitrous acid reacts with primary amino compounds to form diazonium ions, $G\text{-}N_2^+$ (G = organic or inorganic group). Diazonium ions decompose to gaseous nitrogen and other products, the nature of which depends on the structure of the group G. Measurement of the volume of nitrogen evolved from such a system is a means of determining either the relative number of primary amino groups in the sample (by use of excess nitrous acid) or the relative amount of nitrite in a sample (by use of excess primary amino compound). The latter procedure will be used to determine the amount of nitrite in the compounds which you prepare.

The reagent that will be used for the determination of nitrite is sulfamic acid, which can be represented by the formula[3] $H_2N\text{-}SO_3H$. Like other sulfonic acids, it is a strong acid in aqueous solution, and it also contains a primary amino group (or ammonium group in the zwitterionic form[3]). Thus, sulfamic acid serves both to protonate nitrite and to convert it quantitatively to gaseous nitrogen. These consecutive processes are outlined by the equations below.

$$M(NO_2)_6^{4-} \longrightarrow M^{2+}{}_{(aq)} + 6NO_2^-$$

$$NO_2^- + H_3O^+ \longrightarrow HNO_2 + H_2O$$

$$HNO_2 + H_2N\text{-}SO_3^- \longrightarrow N_2 + HSO_4^- + H_2O$$

The nitrogen can be collected by using it to displace water from a calibrated vessel. The exact amount of nitrogen formed can then be calculated by use of the ideal gas law, after making appropriate corrections. Two corrections need to be made: one for the vapor pressure of water, and one for the hydrostatic pressure of the water column in the eudiometer tube (a calibrated gas collection tube) which is used to collect the nitrogen. The first correction is necessary since the nitrogen will be bubbled through water; part of the measured pressure will thus be due to the vapor pressure of water at the temperature of the measurement. The column of water which remains in the tube after collection of nitrogen has ceased exerts a pressure which is proportional to its height, and so must be considered. This hydrostatic pressure can be converted to mmHg (torr) by use of the densities of water and mercury at the temperature of the measurement.

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[3] Solid sulfamic acid would be expected to contain a substantial amount of the zwitterionic form, $^+H_3N\text{-}SO_3^-$.

The total pressure in the eudiometer tube after gas evolution is complete will be equal to the atmospheric pressure ($P_{\text{atmospheric}}$). The atmosphere acts in opposition to forces from three sources:

(1) pressure from $N_{2(g)}$ - represented as P_{nitrogen}

(2) pressure from $H_2O_{(g)}$ - represented as $P_{\text{water vapor}}$

(3) pressure from the mass of the water column - reperesented as $P_{\text{hydrostatic}}$.

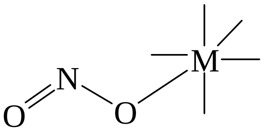
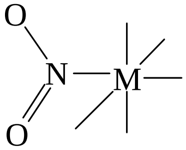
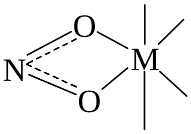
Thus, $P_{\text{atmospheric}} = P_{\text{nitrogen}} + P_{\text{water vapor}} + P_{\text{hydrostatic}}$

The atmospheric pressure will be read during your particular lab period and posted on the blackboard - be sure to record the value before you leave the lab for the day. You will also need to measure the temperature of the water which you use in the gas-collection apparatus, so that you can look up the vapor pressure at that temperature. A table of water vapor pressures at various temperatures is posted in the lab.

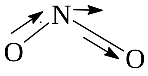
The hydrostatic pressure can be measured by use of a meter stick: measure the height of the water column in the eudiometer tube, from the surface of the water in the beaker to the top of the water column. This gives you a measurement of the hydrostatic pressure in mm of water. To convert to mm of mercury, consider the fact that the atmosphere will support a column of mercury the mass of which is equal to that of the water column which you measure. Thus, division of the density of water at the given temperature by the density of mercury will give you a factor for conversion of mmH_2O to mmHg.

Infrared Analysis of Nitrite Complexes - Background

The nitrite ion is ambident: it contains more than one type of lone pair for potential coordination to a metal atom. Thus, isomeric complexes having structures such as those shown below are possible.

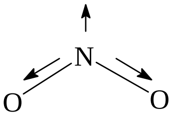




These types of structural isomers can be distinguished by infrared spectroscopy. The free nitrite ion (e.g. in simple salts such as $NaNO_2$) has three fundamental vibrations: a symmetrical stretch (υ_s); an unsymmetrical stretch (υ_{as}); and a bending vibration (δ). The motions which the atoms of the nitrite ion undergo when these vibrations occur are shown in the diagram below. Note that they will all cause a change in the dipole moment of NO_2^-, and so are observable in the infrared spectrum.



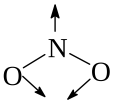
ν_{as}

asymmetric stretching vibration



ν_s

symmetric stretching vibration



δ

bending vibration

In the noncomplexed nitrite ion, only these three fundamental bands are observed in the infrared spectrum. Their values are given in Table II. When the nitrite ion coordinates to a metal, the positions of the bands change due to the change in the nature of the bonding of the -(NO_2) group. In addition, splitting of the bands can occur due to coupling of the vibrations of each -(NO_2) group with other groups in the complex. This results in several absorption bands that overlap to form a wide, intense absorption in which individual bands, when they can be observed, are present as shoulders or as relatively broad individual peaks superimposed on the wider envelope of absorptions.

The positions of υ_s and υ_{as} (and δ, to a lesser extent) are different for each of the possible types of bonding of nitrite to the metal. Typical ranges for these vibrations are given in Table II. The absorptions that you will observe for your samples are very intense, and thus the base of the absorption envelope will fall outside of these ranges; the absorption maxima, however, generally appear where they are expected. You will also observe infrared absorptions due to stretching and bending vibrations of water if your sample is either damp or hydrated.

<u>TABLE II</u>

Compound or Compound Type	υ_s	υ_{as}	δ	cm^{-1}
$NaNO_2$	1328	1261	828	
$M-NO_2$ (nitro complexes)	1250-1350	1400-1420	800-840	
M-O-N=O (nitrito complexes)	1445-1460	1050-1200	810-840	
chelating nitrite	1190-1205	1265-1315	845-870	

EXPERIMENTAL PROCEDURES

A. Synthesis of Complexes

Hazard Notes:

(1) Many of the metal salts, particularly those of barium and nickel, are toxic. Take care not to allow them to contact your skin. Wash your hands thoroughly before leaving the lab at the end of the experiment.

(2) Potassium nitrite (KNO_2) and sulfamic acid (H_2NSO_3H) have similar appearances: both are white, crystalline solids. When weighing these materials, be sure not to inadvertently cross-contaminate the bottles from which the two reagents are taken. Contamination of potassium nitrite with sulfamic acid, or vice versa, produces a large amount of heat and gaseous nitrogen. Bottles which are contaminated in this manner can become very hot and explode from the gas pressure.

Choose a combination of alkaline earth chloride and transition metal(II) chloride from Table I, and weigh out 0.0025 mole of each (note: if the salt is a hydrate, the formula weight of the hydrated salt must be used for the calculation of masses). Dissolve both compounds in a minimum volume (about 2.5 mL) of deionized water. If necessary, the mixture can be gently heated to cause more rapid dissolution.

Weigh out 0.025 mole of KNO_2 and dissolve it in 2.5 mL of water. Slowly add the KNO_2 solution, with stirring, to the metal chloride solution. The complex salt will form rapidly. After the addition is complete, cool the mixture in an ice bath to ensure maximum precipitation of the product. While the mixture is cooling, make a separate solution of about 0.1-0.25 g of KNO_2 in 1.5 mL of water, and cool it to ice temperature.

Decant the supernatant into a funnel containing a small fluted filter paper. Add the 1.5 mL of cold KNO_2 solution to the residual solid in the reaction flask, swirl to suspend the solid, then filter the mixture through the fluted filter paper. After the water has drained, pour two consecutive 5 mL portions of acetone through the filter paper to help dry the solid. After the acetone has drained, open the filter paper, scrape off the solid, and spread it out thinly on a new piece of filter paper to dry. After most of the solvent has evaporated, final drying can be accelerated by placing the solid and filter paper on a radiator register. Thorough drying, both from water and acetone, is important for both the chemical and infrared analyses.

Weigh the dry solid and record the weight for calculation of the percent yield.

B. Chemical Analysis

For the purpose of calculation of the amount of your complex which will give a quantity of nitrogen measurable by the eudiometer tube, assume a formula of $K_2MM'(NO_2)_6$ for your product, then calculate the mass which will produce 50 mL of N_2. Weigh, to 0.001 g, two portions of your product in this mass range. The masses do not have to be exactly the same, or exactly the same as the mass which you calculated, just close. Each must be known to 0.001 g, however, so as to allow you to calculate the formula of your product later. Be sure to save a small amount of your product for infrared analysis.

Place each sample, along with a few glass beads, into a small glass vial. Dissolve 0.5 g of sulfamic acid in 20 mL of water in a 125 mL Erlenmeyer flask. Carefully place one of the vials of complex in the flask - do not allow the vial to tip over.

Stopper the flask with a one-hole rubber stopper which has a rubber tube attached to it.

Fill a eudiometer tube with water and invert it in a large beaker of water; use a buret clamp to hold the tube after it is inverted. Be sure that all gas has been expelled from the tube. Lead the rubber tube from the reaction flask underneath the water in the beaker and into the eudiometer tube.

Shake the flask so as to tip over the vial which contains the nitrito complex. Vigorous evolution of nitrogen will occur. Wait about ten minutes to ensure complete reaction; swirl the flask occasionally.

Record the following measurements for your calculation of the formula of your complex: (1) volume of gas in the eudiometer tube; (2) height, in cm, of the water column in the eudiometer tube; (3) the barometric pressure; (4) room temperature; and (5) temperature of the water in the beaker.

Repeat the analysis with your second sample of complex.

When you wash your glassware, do not dump the glass beads down the drain or into the sink. Wash them and place them in the container which is provided in the lab.

Place any of your product which is left over into a labeled, corked test tube and turn it in to your instructor.

Infrared Analysis

Grind a small amount of your product with dry KBr in the Wig-L-Bug or in in an agate mortar. One of your instructors will press the sample into a pellet and record the infrared spectrum.

Report

Use the results of the chemical analysis to decide the degree to which your product is hydrated (if it is hydrated at all), and calculate the empirical formula of the hydrate: $K_2M'M(NO_2)_6 \cdot xH_2O$ (note: x = 0 if your product is not hydrated). Show all of your calculations in a neat, clear, and detailed manner.

After you have determined the formula of your product, calculate the percent yield.

On the basis of the infrared spectrum of your product, decide in what manner the nitrite ligands are bound to the transition metal. Provide a clear rationale for your conclusions.

Pre-Lab Questions - Nitrite Complexes

1. Show the method by which you plan to calculate the masses of reactants which you will use for this experiment.

2. What percentage of the nitrogen evolved in the analysis for nitrite is derived from nitrite?

3. What is a labile complex? How is the phenomenon of lability related to this experiment?

4. What are the features for which you will be searching when you analyze the infrared spectrum of your product?

Inorganic Chemistry Laboratory Report - Hexanitritometallates

Name:______________________________ Lab section (day):________ Date:__________

1. Balanced equations and observations for all reactions which occurred, in order of occurrence.

2. Calculations for the Chemical Analysis

3. Infrared analysis - perform this analysis on the spectrum itself; attach the spectrum to this sheet.
Show how you used the spectrum to assign the bonding mode of nitrite in your sample.