

Syllabus

CHM 402
Physical Inorganic Laboratory
Spring, 2019

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Purpose: This laboratory focuses on the preparation and physical characterization of inorganic compounds with an emphasis on transition metal complexes. The experiments are designed to illustrate fundamental principals in both theory and spectroscopic techniques. The use of your 401 text and **additional literature references** for each experiment are **mandatory**, as these handouts only give you enough information to get started on any experiment. Additional library work will be necessary and should be fully cited in your reports. You **must** come into the laboratory each week with a detailed procedure in your notebook, including required weights and important safety information (see next page).

Experiments:

- A: Preparation of potassium trisoxalatochromium(III).
- B: Preparation of pentaamminenitritocobalt(III) chloride.
- C: Preparation of dichromiumtetraacetate dihydrate.
- D: Preparation of Copper(I) Chloride
- E: Preparation and study of $[(\text{CH}_3\text{CH}_2)_2\text{NH}_2]_2[\text{CuCl}_4]$
- F: Preparation and Characterization of Metal Phthalocyanines

Instrumentation: Infrared spectroscopy
UV-Visible spectroscopy.
Electron Spin Resonance Spectrometry

Grading: Six reports are required for the course. These are to be in the style of a communication (Expts A-E) or full paper (F) submitted to *Inorganic Chemistry*. They should include detailed procedures, including any variations from the given instructions, the original data with analysis of the results and answers (in good English) to the questions posed in each experiment. Reports are due **1 week** after you have completed the experiment. Include with your report the pertinent section of each of your literature references (**no Wikis!**) Late reports will be penalized 10% per week. **Independent work is expected!** The lab reports are on the following experiments:

Experiments A-E, 10 % Each
Final project – Metal phthalocyanine complexes (25%).

The remaining 25% of the grade is our evaluation of your laboratory performance, preparation, and lab notebook.

Schedule: The Lab will be open Wednesday and Friday at 1pm

You may come on the “other” day to finish, repeat or make-up experiments

| Date | Jamie Laura | Paul Chris | Cassie Gabriel | Kate Ryan | Adriana | Melissa | |
|--|--|---------------|-------------------|--------------|---------|---------|--|
| January 23 (Wed) | Introduction to the Course | | | | | | |
| January 30/Feb1 | A1 | B | C1 | E1 | D | D | |
| February 6/8 | A2 | C1 | C2 | E2 | B | E1 | |
| February 13/15 | B | C2 | D | D | A1 | E2 | |
| February 20/22 | C1 | D | E1 | A1 | A2 | B | |
| February 27/Mar1 | C2 | E1 | E2 | A2 | C1 | A1 | |
| March 6/8 | D | E2 | A1 | B | C2 | A2 | |
| March 20/22 | E1 | A1 | A2 | C1 | E1 | C1 | |
| March 27/29 | E2 | A2 | B | C2 | E2 | C2 | |
| April 3/5 | F | F | F | F | F | F | |
| April 10/12 | F | F | F | F | F | F | |
| April 17/19 Presentation Preparation | F | F | F | F | F | F | |
| April 24/26 | Group Presentation of Project: Lab Cleanup, Checkout, All Reports Due | | | | | | |

Experiments:

A1: Preparation of $K_3Cr(ox)_3 \cdot 3H_2O$.

A2: UV-Vis spectra of $K_3Cr(ox)_3 \cdot 3H_2O$.

B: Preparation of $Cr_2(C_2H_3O_2)_4 \cdot 2H_2O$.

C1: Preparation and IR spectrum of $[Co(NH_3)_5NO_2]Cl_2$ isomer 1.

C2: Preparation and IR spectrum of $[Co(NH_3)_5NO_2]Cl_2$ isomer 2.

D: Preparation of Copper(I) Chloride

E1: Preparation of $[(CH_3CH_2)_2NH_2]_2[CuCl_4]$

E2: Spectroscopy of $[(CH_3CH_2)_2NH_2]_2[CuCl_4]$

F: Project—preparation and characterization
of metal-phthalocyanine complexes.

*Prior to coming to the lab you must have a written procedure in your notebook to follow with experimental details such as exact volumes, masses, or molarities of reagents that you will use. You will need to prepare all reagents from commercially available sources (e.g. concentrated acids) that are provided in the lab or by the stockroom so you should check the label on the bottles (and calculate amounts) the week before each experiment. You also **must** have an SDS/(MSDS) for each reagent that you will be using in your notebook prior to starting any lab work.*

Reports are due the lab period after completion of each experiment.

In conversation and reports, refer to experiments, reagents and products by name not formulas or “A-F”.

Format for Formal Reports Written in the Style of an ACS Journal

Title page with your name, affiliation, E-mail

Abstract

The Abstract is a brief overview of the results obtained from the research activity. The Abstract should be no longer than 150 words. You should not use abbreviations in the Abstract, unless they are defined.

Introduction The Introduction provides the relevance and context of the research and the goals that were sought. This section also gives the reader an idea of previously done research in the area of study, so is typically **heavily referenced to the literature**.

Experimental Section This part of the paper provides all experimental details. There should be sufficient information given so that anyone could reproduce the results. Do not just repeat the procedure in the handout: give all details of what you have done, including actual weights.

Results This section is the meat of the report and should include representative data for all measurements or calculations done. There should be enough data reported so that the reader can understand the conclusions that were reached. Graphical data should be labeled as Figures (Fig. 1, Fig. 2, etc) and each Figure should have a caption.

Discussion The Discussion section is used to explain the data and lead the reader to the conclusions drawn from the study. The Results and Discussion sections can be combined into one section, if appropriate. This is normally where you will address the questions posed in each experiment.

Conclusion This is a brief reiteration of the conclusions drawn from the study.

References This section has the literature citations that are referenced in text. Each citation is numbered and listed in order given in text. If a reference is cited more than once in text, only the first number is used. The style for citations is: Author1, Author2, ..., *Journal Title (usually abbreviated)*, Year, *Volume*, pages. Note the use of Bold and Italic type, which is part of the ACS style. **Note that the references given in this syllabus are for the procedures. They do not give sufficient background for your report.**

Supplementary Material: Attach the page(s) of each of your references that justifies each citation with key phrases highlighted..

The writing style for papers includes each Section Heading being offset and in **bold** type.

Format for Communications Written in the Style of an ACS Journal

Communications are short papers that report only one or two key results. The style of a Communication is the same as a formal paper but there are no section headings except for the Abstract and References are optional and each section is usually no more than one or two paragraphs.

PLAGAIRISM WILL NOT BE TOLERATED! Be sure to paraphrase all the material you reference. Exact quotes are rarely appropriate in a scientific presentation (even if in "...").

Electronic Spectroscopy

Transition metal compounds display a wide variety of colors and many of these compounds are used as artist's pigments (e.g., copper phthalocyanine, Prussian blue, and Thénard's blue are all various shades of blue). The color of these compounds is due to electronic transitions induced by the incident light, causing absorption at certain wavelengths, depending on the structure and bonding in the molecule. UV-Visible spectroscopy is used to quantitate the absorption properties of molecules.

The electronic transitions of transition metal compounds can be categorized into three types: charge transfer, d-d spin-allowed, and d-d spin-forbidden. Charge transfer bands occur when the excited electron moves from a metal centered orbital to a ligand-centered orbital (metal-to-ligand charge transfer - MLCT) or when the excited electron moves from a ligand-centered orbital to a metal centered orbital (ligand-to-metal charge transfer - LMCT). MLCT bands are more common than LMCT. Spin-allowed and spin-forbidden d-d transitions find the excited electron moving from one d orbital to another d orbital. In the spin-allowed transition the spin quantum number (or more accurately, the spin angular momentum) in the ground and excited states are the same while in the spin-forbidden transition the spin state changes during the excitation. These three types of transitions are distinguished by the molar absorption coefficient (or "extinction coefficient," ϵ in the Beer-Lambert law: $A = \epsilon bc$): charge transfer bands have large ϵ , generally in the range of 1000 to 10000 L/mol-cm. Although d-d transitions in truly octahedral fields are forbidden by symmetry (since d orbitals have *gerade* inversion symmetry and the electric vector is *ungerade*), vibronic coupling allows the transitions to be observed but with reduced intensity. Spin-allowed d-d transitions have ϵ values of well below 10 L/mol-cm for truly octahedral complexes and up to 100 for nearly octahedral ligand fields - eg for a $M(L-L)_3$ complex where the symmetry is reduced from O_h to D_3 . Tetrahedral complexes, which have no center of symmetry can have extinction coefficients up to about 1000. Spin-forbidden bands have ϵ values typically less than 1 L/mol-cm. Spin-forbidden bands are often not observed in solution except for high spin d^5 systems, which have no spin-allowed transitions. UV-Vis spectroscopy can be used to distinguish octahedral from tetrahedral geometries. It is important to report both peak positions and molar extinction coefficients for electronic spectra.

UV-Vis spectra can be used to investigate both the geometric structure and the electronic structure (i.e., the nature of the bonding) in transition metal complexes. Most spectra are measured in solution and this leads to broad absorption bands that give rise to few structural details. Because of this, only the most general structural conclusions (as described above) can usually be deduced. One exception to this statement is the optical titration experiment where a series of spectra are recorded as a function of added reactant (usually the ligand is added to the metal). The observation of isosbestic points (wavelengths where all of the spectra intersect, independent of the concentration of the added reactant) means that there is a well defined limit to the number of absorbing species in solution and with this information the structure of the solution species can often be deduced.

The primary use of UV-Vis spectra for transition metal complexes is the elucidation of electronic structure parameters. Generally this means the crystal field parameter Δ_0 (10Dq) and sometimes the Racah interelectron repulsion constant B. These values are presented graphically in the **Tanabe-Sugano diagrams**. For d^1 , d^4 (high spin), d^6 (high spin), and d^9 complexes a single spin-allowed d-d transition is observed with energy 10Dq. High spin d^5 complexes have no spin-allowed d-d bands so are lightly colored unless charge transfer bands dominate the spectrum. For d^3 and d^8 octahedral complexes, three spin-allowed transitions are predicted at energies given by:

:

$$\nu_1 = 10Dq$$

$$\nu_2 = 7.5B + 15Dq - \frac{1}{2}\sqrt{225B^2 + 100Dq^2 - 180BDq}$$

$$\nu_3 = 7.5B + 15Dq + \frac{1}{2}\sqrt{225B^2 + 100Dq^2 - 180BDq}$$

where all the parameters are in units of cm^{-1} . [you will note from the units that ν is neither energy (joules) or frequency (sec^{-1}) but actually wave number = $1/\lambda$. However, it is usually called "frequency" here and in IR spectra.]

If all three transitions are observed, $10Dq$ can easily be found from ν_1 and B can be found from $15B = \nu_3 + \nu_2 - 3\nu_1$. Often a charge transfer band will obscure ν_3 so that B must be found from

$$3B = \frac{(\nu_2 - 2\nu_1)(\nu_2 - \nu_1)}{(5\nu_2 - 9\nu_1)}$$

If the complex has a d^2 or d^7 (high spin) configuration, three bands are also expected and are given by:

$$\nu_1 = -7.5B + 5Dq + \frac{1}{2}\sqrt{225B^2 + 100Dq^2 + 180BDq}$$

$$\nu_2 = -7.5B + 15Dq + \frac{1}{2}\sqrt{225B^2 + 100Dq^2 + 180BDq}$$

$$\nu_3 = \sqrt{225B^2 + 100Dq^2 + 180BDq}$$

where, again, all parameters are in units of cm^{-1} . Here $10Dq$ is found from the difference of the first two bands, $10Dq = \nu_2 - \nu_1$, and B is found from $15B = \nu_3 + \nu_2 - 3\nu_1$. If only the first two transitions can be observed, then B can be found from

$$3B = \frac{(\nu_2 - 2\nu_1)\nu_1}{(9\nu_1 - 4\nu_2)}$$

For complexes with other electron configurations no simple formulas exist to find the crystal field parameters.

The crystal field strength, $10Dq$, measures the splitting between the t_{2g} and e_g orbitals and depends on both the metal ion and the ligand. The spectrochemical series denotes the variation of $10Dq$ as a function of ligand with weak ligands such as Cl^- or H_2O leading to small values of $10Dq$ and stronger ligands like NH_3 or CN^- giving larger values of $10Dq$. The interelectron repulsion constant B is usually compared to the free ion value as

$$\beta = B_{\text{complex}}/B_{\text{free ion}}$$

Bonding reduces the interelectron repulsion in a complex relative to the free (gas phase) ion (this happens because the metal d electrons expand to bond to the ligands and electrons that are farther apart from each other repel each other less) so that β is always less than 1. The value of β also varies from ligand to ligand and this series is known as the nephelauxetic series, which is similar to but not identical to the spectrochemical series.

Experimental reports of UV-Vis data are not complete unless both the peak position and the molar absorptivity of each peak is given. A solution should be prepared so that the absorbance is between 1.5 and 2.0 and analytically diluted 4 or 5 times so that the most dilute concentration is at least 10 times smaller than the initial concentration. The spectrum is recorded at each dilution and the absorbance of each peak is plotted as a function of concentration. This plot should yield a straight line with a slope of ϵ (for a 1 cm cell) and an intercept of 0. If the slope has curvature, then the either experimental technique needs to be improved or the compound is reacting with solvent, itself, or perhaps air. To calculate Dq and/or B , the peak positions must be identified as spin-allowed $d-d$ transitions in an octahedral environment and then converted to energy units, usually cm^{-1} .

References

R. S. Drago, *Physical Methods for Chemists*, Saunders, Philadelphia, 1977, p. 411.

P. Atkins *et al*, *Shriver and Atkins Inorganic Chemistry*, 5th ed., W.H. Freeman, New York **2009**;
6th ed., **2014**, chapter 20.

Infrared Spectroscopy

Infrared spectroscopy is one of the most important physical characterization techniques used by the inorganic chemist. It can be used for identification of compounds, elucidation of bonding characteristics, and for quantitation of species. The most frequent application of IR spectroscopy is the identification of a compound, a particular ion or chemical functionality.

Infrared absorptions arise because vibrations in the molecule that cause a change in the dipole moment of the molecule absorb the incident radiation. In a (heteronuclear) diatomic molecule a single vibrational peak may be found in the IR spectrum since only one vibration exists. This vibration can be modeled by considering the bond as a spring (a harmonic oscillator) and then use of Hook's law gives the energy of the vibration in terms of the spring constant. The molecular parameter associated with the spring constant is called the force constant and is a measure of the bonding in the molecule. Hook's law also involves the mass of the atoms connected to the end of the spring so that vibrational frequencies are identified with two characteristics: atomic masses and bond strength. In more complex molecules these force constants are similar for a series of the same atoms bonded in the same fashion (e.g., the force constants for a C-C single bond are similar for most molecules) so that vibrational peaks for a given type of bonding always show up in the same region of the spectrum; for example, CO absorbs in the 1700 to 2150 cm^{-1} region for virtually all complexes. These are called group frequencies and are useful for structure determination of new compounds.

Two types of group frequencies are especially important to the study of metal complexes: metal-ligand stretches and carbonyl stretches. Both occur in spectral regions with few other absorptions (metal-ligand stretches are found in the 200-550 cm^{-1} region and CO as noted above) so that they are observed with few interferences.

Since bond strength and atomic masses determine vibrational energies, the position of the metal-ligand stretching depends on both the metal atom and ligand atom involved. As the masses of the bonded atoms increase the vibrational frequency decreases; as the bond strength increases so does the IR absorption frequency. Two of the most common types of ligands are ammonia (ammine) and halide. The metal-nitrogen stretch usually falls in the 400-500 cm^{-1} region (depending on the metal) and the metal-halide stretch varies considerably, depending on both the metal and the halide. Typical examples are given in Table 1. Note that the interactions in Table 1 are for coordinate covalent interactions (dative bonds with two-electron donors) and are, thus, weaker than electron pair bonds. Modern Fourier Transform IR Spectrometers usually have a lower limit of around 600 cm^{-1} and these interactions are not seen directly.

Table 1

| $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ | Co-N (cm^{-1}) | Co-X (cm^{-1}) |
|---|---------------------------|---------------------------|
| X=F | 498, 480, 438 | 343 |
| X=Cl | 498, 476, 416 | 272 |
| X=Br | 497, 475, 410 | 215 |
| X=I | 498, 473, 406 | 168 |

The data in Table 1 (taken from Nakamoto) clearly shows the mass effect of varying the halide while demonstrating the invariance of the bonding to the ammine ligands. Despite the existence of five Co-N bonds only three Co-N stretches are observed: one of the possible Co-N stretches is not IR active (it does not cause a change in the dipole moment of the molecule) while two other vibrations are degenerate (i.e., of the same energy), thus only three vibrational peaks are expected - as observed. These conclusions can be found by using the symmetry of the molecule and group theoretical techniques.

Carbon monoxide (CO) is a common ligand, in organometallic complexes, and has a strong IR absorption in the region where few other groups absorb. The metal-CO bond is the classic example of backbonding where the metal d electrons donate density into the vacant π^* orbitals of the CO creating a stronger metal-carbon bond and a weaker carbon-oxygen bond. Free CO has an IR absorption at 2155 cm^{-1} while the CO frequency is always lower in complexes. CO can bond to metals in two fashions: as a terminal ligand to a single metal atom or as a bridge between two (or more) metal atoms. The IR frequencies between these two types of bonding modes are readily distinguishable. Terminal CO groups absorb in the 2000-2100 cm^{-1} region while bridging CO groups absorb between 1800 and 1900 cm^{-1} (not surprisingly, more like organic carbonyls). This can be useful for distinguishing structural features in multimetal complexes. For example, dimanganesedecacarbonyl, $\text{Mn}_2(\text{CO})_{10}$, has IR peaks at 2046, 2015, and 1984 cm^{-1} , all indicative of only terminal carbonyls which implies that the two metal atoms are linked solely by a metal-metal bond. In contrast, dicobaltoctacarbonyl, $\text{Co}_2(\text{CO})_8$, has absorptions at 2075, 2064, 2047, 2035, 2028, 1867, and 1859 cm^{-1} indicating the presence of two bridging CO moieties (this was confirmed by other structural methods).

All of the samples we synthesize in CHM402 are solids. The instrument we use is a Shimadzu IRTracer-100 with an Attenuated Total Reflectance (ATR) accessory. In this technique, the sample is placed in contact (under pressure) with a crystal (e.g. diamond) and incident IR radiation interacts at the interface on its way to the detector. The crystal has a very small cross section (~2mm) and must be kept scrupulously clean.

References

E. A. V. Ebsworth, D. W. H. Rankin, S. Craddock, *Structural Methods in Inorganic Chemistry*, Blackwell Scientific, Oxford, **1987**.

K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 4th edition, **1986**.

P. Crews, J. Rodriguez, M. Jaspars, *Organic Structure Analysis (2nd ed)*, Oxford, New York, **2010**.

Electron Spin Resonance Spectroscopy (ESR) aka Electron Paramagnetic Resonance Spectroscopy (EPR)

Electron Paramagnetic Resonance (EPR) spectroscopy (also known as electron spin resonance, ESR) is a resonance technique analogous to NMR spectroscopy. The unique feature of EPR spectroscopy is that the resonance is of unpaired electrons in a compound, which make EPR spectroscopy an excellent tool for measuring the electronic properties of many transition metal complexes.

The resonance condition for an unpaired spin is given by

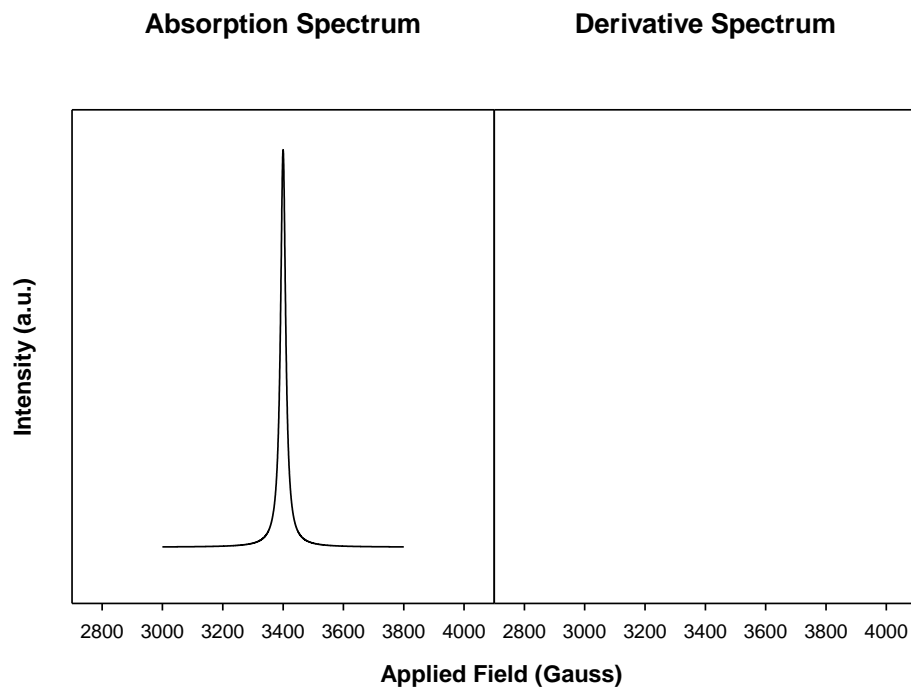
$$\Delta E = h\nu = g\beta H \quad (1)$$

where h is Planck's constant ($= 6.627 \times 10^{-34} \text{ J}\cdot\text{s}$), ν is the frequency in Hz, β is the Bohr-magneton ($= 9.274 \times 10^{-24} \text{ J/T}$), H is the applied magnetic field in T ($1 \text{ T} = 10^4 \text{ gauss}$), and g is known as the g -factor. The g -value is a fundamental constant for a free electron ($g = 2.00229$) but the value varies in molecules and is an indirect measurement of bonding characteristics. In organic free radicals the g -factor normally is quite close to 2 but in transition metal complexes g -factors can range from 1.6 to 6, depending upon the electron configuration and the symmetry. The g -factor is analogous to the chemical shift in NMR spectroscopy. In low symmetry environments the g -factor has different values in different directions (i.e., the g -factor is a tensor quantity), which leads to multiple g -values in solids. In liquids the measured g -factor is an average over all directions so is observed as a single value.

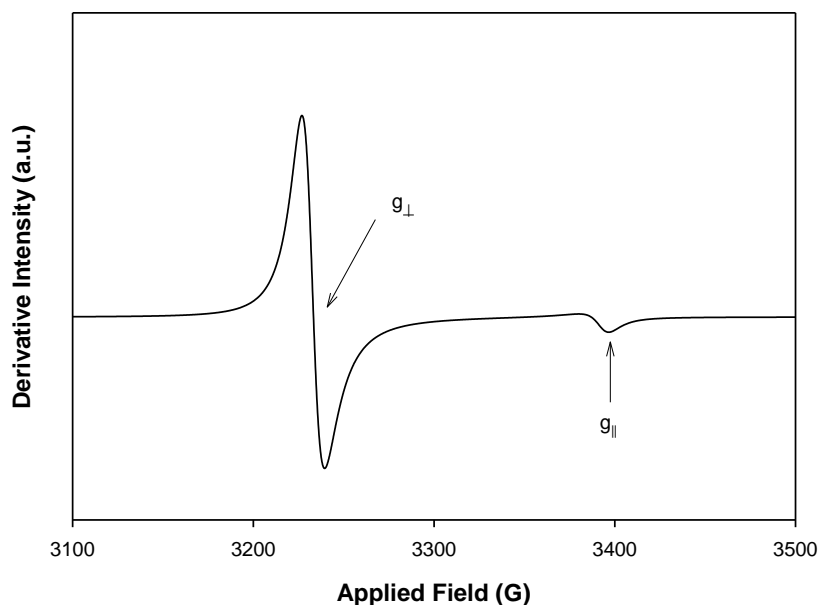
An additional feature is coupling between the electron spin and nuclear spins, known as hyperfine coupling. Hyperfine coupling is analogous to spin-spin splitting in NMR spectroscopy but there are a larger number of isotopes available for hyperfine coupling, including those with nuclear spin, I , greater than $1/2$. When an electron spin couples to a nuclear spin the spectrum is split into $2I+1$ peaks, where I is the sum of the nuclear spin over all equivalent nuclei. For example, ^{59}Co (100 % natural abundance) has $I = 7/2$ so EPR spectra of cobalt complexes are split into 8 peaks. When there are multiple nuclei the EPR spectrum can be very complex. Copper complexes have hyperfine splitting from two types of copper: ^{63}Cu ($I = 3/2$, 69 % abundant) and ^{65}Cu ($I = 3/2$, 31 % abundant), which gives spectra with two sets of 4 peaks in, roughly, 2:1 intensity ratio. If there are multiple types of atoms with nuclear spins, all of them can contribute to splitting. For example, the EPR spectrum of a cobalt complex with four equivalent nitrogen atoms (^{14}N , $I = 1$, 99+ % abundant) bonded to the cobalt would be expected to have $(2I_{\text{Co}} + 1) \times (2I_{\text{N}} + 1) = (2 \cdot 7/2 + 1) \times (2 \cdot 1 + 1) = 72$ peaks. The hyperfine coupling is proportional to the overlap between the spin-bearing and the coupled nucleus so is a measure of the covalency in a bond.

One of the experimental limitations in EPR spectroscopy is that many paramagnetic samples can not be observed at room temperature. This occurs because spin-spin relaxation (i.e., a nearby spin causes the excited spin to quickly return to the ground state) causes linewidths to be extremely broad. This is especially true for metal ions with integer spin ($S = 1, 2, 3, 4$, etc.). Half-integer spins ($S = 1/2, 3/2, 5/2$, etc.) typically can be observed at room temperature but if the concentration of spins is too high, then again, linewidths can be broad leading to undetectable spectra. Diluting a material with a half-integer spin into a diamagnetic matrix often will give measurable spectra.

Since transitions in electron spin are of higher energy than those of nuclear spin, the frequencies involved are in the microwave region (around 9.5 GHz for our "X-band" spectrometer) rather than the radio wave region employed in NMR. While the frequencies of radio waves are easily varied, this is not true for microwaves. Thus in a typical EPR experiment the excitation frequency is held constant and the magnetic field is swept. For a sample with $g = 2$ the resonance field is expected at $H = h\nu/g\beta = (6.627 \times 10^{-34} \text{ J}\cdot\text{s})(9.5 \times 10^9 \text{ Hz}) / (2)(9.274 \times 10^{-24} \text{ J/T}) = 0.34 \text{ T} = 3400 \text{ gauss}$ so this is the region that an initial sweep is run. Normally EPR spectra are represented as derivatives rather absorption maxima. An example comparing the absorption lineshape to the derivative lineshape is shown below. The resonance positions in derivative spectra are at the zero crossings (with the exception of powder patterns, discussed below).



In randomly oriented solid samples (powders or frozen solutions) the observed EPR spectrum is a combination of the spectra from all orientations. This gives rise to an unusual phenomenon – a derivative spectrum that has an absorption maximum or minimum. An example of this is shown in the figure below. Note the absorption shape (as a



downward peak) at $H \approx 3400$ G. This is a typical spectrum for a tetragonal complex. If hyperfine splitting is possible, then each of the features may be split with g_{\perp} having derivative lineshapes and g_{\parallel} have absorption lineshapes. If g_{\parallel} is larger than g_{\perp} , then the absorption feature is a maximum at a field lower than the derivative feature. In rhombic complexes, where $g_x \neq g_y \neq g_z$, the spectrum will display a positive absorption, a derivative, and a negative absorption lineshape.

Powder EPR spectra of transition metal complexes can range from relatively simple to quite complex. For example, compounds containing Cr^{3+} ($S = 3/2$; ^{53}Cr , $I = 3/2$, 9.5 % abundant) are usually quite simple: an absorption maximum, a derivative, and an absorption minimum (assuming a low symmetry environment). There usually is no hyperfine splitting observed because the ^{53}Cr nucleus is in low abundance and has a small nuclear magnetic moment, which means that the hyperfine splitting is less than the linewidth. In contrast, copper complexes often give very complex powder patterns. Both ^{63}Cu and ^{65}Cu ($I = 3/2$) can give hyperfine splitting on both the derivative and absorption features, leading to spectra with 12 or more lines to assign.

In reporting the results from EPR spectra, the experimental details must include the frequency and temperature that the sample was run at. Interpretation of spectra must include assignment of g-values and, where appropriate, hyperfine constants. Typically these are reported in a table if more than one compound was measured.

In addition to the references below, you will be provided with information to help you understand the operation of our instrument. You must study these handouts before making arrangements to do your EPR experiments.

References:

P. Atkins *et al*, *Shriver and Atkins Inorganic Chemistry*, 5th ed., W.H. Freeman, New York **2010**, Section 8.6
[Shriver *et al* *Inorganic Chemistry*, 6th ed., W.H. Freeman, New York **2014** Section 8.7]

J.A. Weil, J.R. Bolton and J. E. Wertz, *Electron Spin Resonance Elementary Theory and Practical Applications*, J. Wiley & Sons, New York, **1994**.

A: Preparation of Potassium Trioxalatochromium(III) Trihydrate

Oxalate serves as a simple and easily manipulated bidentate ligand. Trioxalato complexes of transition metal ions have been known for many years and are generally readily prepared. The trioxalatoiron(II) complex is well known since it is often used to measure the amount of light available in photochemical experiments. The trioxalatochromium(III) complex has been used for the selective precipitation of glycine from a mixture of amino acids. Trioxalato compounds are also optically active and are sometimes used to demonstrate this effect.

In this experiment a very simple procedure to prepare trioxalatochromium(III) is used. The beauty of this preparation is that the complex of interest is the only nonvolatile product so that isolation of the desired material is trivial. The starting material, dichromate, is a common oxidizing agent and is used in a number of organic oxidations. Variations on the preparation described here include the addition of an organic alcohol that has two effects: the rate of the reduction of the Cr(VI) is accelerated and an isolable ketone is formed. The Cr(III) product is a typical example of d^3 materials: stable and substitutionally inert. The sample prepared here will be used in subsequent experiments where various physical properties will be measured.

Experimental

To 30 mL of water add 1.80 g of oxalic acid dihydrate and 0.75 g of potassium oxalate monohydrate. Gently heat this until all of the oxalic acid is dissolved. To this solution, slowly add 0.60 g of potassium dichromate (add this a spatula tip-full at a time to allow the vigorous bubbling to subside between additions). After all the dichromate has been added, heat the solution to boiling and evaporate the solution nearly to dryness. Cool and isolate the product. Dry in air and record the yield. Measure the UV-vis spectrum (in H_2O) from 190 to 1100 nm at several (known) concentrations. You will need to run two sets of concentrations: a higher concentration for the visible region and a lower concentration for the UV region. Run at least 5 concentrations in each spectral range in order to obtain good molar extinction coefficients.

Report

Write your report in the style of a Communication being sure to address the following: Include the balanced equation and calculate the per cent yield. Report the electronic absorption maxima and molar extinction coefficients (show the Beer's law plot for each peak maximum), assign the nature of each transition (CT or d-d), and calculate the crystal field parameter Dq and the Racah parameter B (in wavenumbers). Based on your Dq and B , calculate the expected absorption maxima for ν_1 , ν_2 , and ν_3 . How well do these match the experimental spectra? Why do you think this compound will precipitate glycine but not other amino acids?

Reference

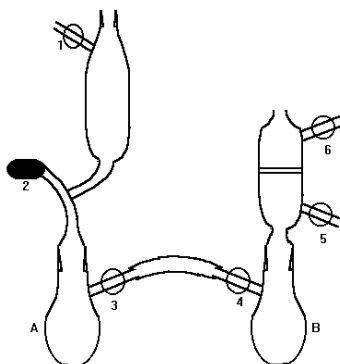
J. C. Bailar and E.M. Jones in H. S. Booth, ed., "Inorganic Syntheses," McGraw-Hill, New York, **1939**, vol. 1, p. 35-37.

B: Preparation of $\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_4 \cdot 2\text{H}_2\text{O}$

Chromium(II) acetate is the classic example of a metal-metal quadruple bond. The acetate ligands act as bridges to help maintain the structure but the d^4 electron configuration of Cr(II) is ideally set up to form the quadruple bond. The waters act as axial ligands for each chromium so that the metal is six coordinate. These axial ligands are sufficiently labile so that they can be replaced by other ligands to modulate the characteristics of the metal-metal bond. Because $\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_4 \cdot 2\text{H}_2\text{O}$ is air sensitive (Cr^{2+} is easily oxidized to Cr^{3+}), the synthesis and handling of the material must be done under a blanket of nitrogen. A whole set of special glassware, called airless ware or Schlenkware, has been developed that allows for the manipulation of reactions and compounds under inert atmosphere on the benchtop without expensive dryboxes. This experiment uses benchtop inert atmosphere techniques to prepare the title compound.

Experimental

Setup the apparatus shown below (flasks A and B are connected by tubing). Into flask A add 1.5 g $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 1.2 g mossy zinc, and 5 mL water. Into flask B add 9 g of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ in about 8 mL of water. Degas each of these with nitrogen gas for about 5 minutes. Seal flask B from the atmosphere and then add 5 mL of



6 M HCl to the addition funnel. Connect the N_2 feed to valve 1 and briefly flush out the funnel, then turn the gas off and seal the top of the funnel off. Make sure that valves 3 and 4 are open and then add a very small amount of the HCl solution to the Zn/ CrCl_3 mixture and then open valve 5. Continue adding the HCl slowly so that the reaction in flask A does not become too vigorous. After the HCl has been completely added, again start the N_2 gas bubbling slowly. The solution in flask A should be clear robin's egg blue (if it is not add more HCl). Carefully tilt flask A so that the solution is poured into flask B through valves 3 and 4. Flask B may become warm at this point; if necessary, cool on an ice bath. Move the N_2 feed to valve 5, close valve 4 and remove flask A and the addition funnel. After precipitation of the product is complete, invert flask B to initiate the filtration using the N_2 gas to feed through the precipitate. To wash the precipitate, set the apparatus upright, add 10 mL of ice-cold, N_2 degassed water through the top of the filter. Invert and filter again. Repeat this process 3 more times with ice-cold, degassed water, then with one wash of 10 mL of 95% ethanol, and then finally one 10 mL wash with ether. When the product is dry, remove the filter, seal both ends (be sure valve 6 is open at this point), close valves 5 and 6 and turn off the gas. Weigh the sealed filter (use the same stoppers that you did when preweighing the empty funnel) and record the yield. Transfer the solid product to a vial in a glove bag filled with nitrogen and seal the vial tightly with parafilm.

Report

Write your report in the style of a Communication being sure to address the following: Write your report in the style of a Communication being sure to address the following: Write out balanced equations for the reactions that occurred and report the percent yield of the final product. Draw the structure of the product and comment on its (observed or potential) reactivity.

Reference

W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Waveland Press, **1991**, Prospect Heights, IL, 442-443.

C: Preparation of $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$

Pentaammine complexes of trivalent cobalt are classic coordination compounds that can be prepared fairly readily. Nitrite is an especially interesting ligand to complete the coordination sphere because it can bond through either an N atom or an O atom. Thus, $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ has two linkage isomers. In this experiment both isomers will be isolated and IR spectroscopy will be used to distinguish them.

Experimental

Dissolve 1.0 g of ammonium chloride in 6 mL of concentrated aqueous ammonia in a 50 mL Erlenmeyer flask and stir this with a hotplate–stirrer. Next, add 2.0 g of finely powdered $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in small portions. Continue stirring and add 1.6 mL of 30% H_2O_2 dropwise with a pipet. When the vigorous reaction has subsided, slowly add 6 mL of concentrated HCl; use the hotplate to maintain the temperature near 85 °C for an additional 10 minutes and then cool to room temperature. Filter off the $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ product and wash it with ice–cold water, followed by ice–cold 6M HCl and then air dry and record the yield. Measure the IR spectrum. Take 1.0 g of the dried $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (if you did not obtain this much, scale back appropriately) and dissolve it in a solution composed of 1.5 mL of concentrated aqueous ammonia in 16 mL of H_2O . Heat this to 60–70 °C and then filter off any cobalt oxide that may have formed. Cool the filtrate to 10 °C and then titrate with 2M HCl until the solution is just neutral to litmus. Add 1.0 g NaNO_2 followed by 1 mL of 6M HCl. Cool the solution on an ice bath for 1–2 hours or refrigerate overnight. Filter the product, isomer 1. Wash this with ice water and alcohol, air dry (Do not heat!) and determine the yield. Record the IR spectrum of isomer 1 as quickly as possible after the product has dried since this isomer has a limited lifetime. Take about half of your isomer 1 product and dissolve it in a minimum of hot water that has had a few drops of concentrated aqueous ammonia added to it; allow the solution to start cooling slowly and then add an equal volume of concentrated HCl. Allow the solution to cool to room temperature, filter the isomer 2 product, wash with alcohol, and air dry and find the yield. Again measure the IR spectrum.

Report

Write your report in the style of a Communication being sure to address the following: Write balanced equations for all reactions, including the formation of the cobalt oxide impurity. Report the percent yields at each step. Identify the IR bands associated with the NO_2^- ligand and the Co–N stretches. Determine the geometry of isomers 1 and 2 and discuss the supporting IR evidence and cite the literature references that you use to make the IR peak assignments.

Reference

W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Waveland Press, Prospect Heights, IL, **1991**, p. 462.

D: Preparation of Copper(I) Chloride

The most common oxidation state for copper is +2, but the mono- and trivalent states are also known. Trivalent copper is stabilized by strong donor ligands including periodate and tellurate ions and nitrogen-containing macrocycles. The aquacopper(I) ion is unstable with respect to disproportionation so that solutions of Cu^+ cannot exist at concentrations higher than about 0.01M. However, precipitation of (e.g.) the chloride, iodide (an important step in the analytical determination of copper in brass) or cyanide results in solid copper(I) salts of very low solubility.

Experimental

Mix 13 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with about 20 mL of water and slowly add (use a magnetic stirrer) a solution of 10 g sodium sulfite in 50 mL of water. A suspension of CuCl will be formed. Add this suspension to a liter of water containing 2 mL of concentrated HCl and 1 g of sodium sulfite. Stir well for about a minute and let it stand until the solid has settled to the bottom of the beaker. Remove, and set aside about 25 mL of the liquid, and decant most of the rest (into the waste bottle!) Quickly wash the precipitate in a sintered glass crucible using a total of 500 mL of water containing 1 mL of HCl and 0.5 g of Na_2SO_3 . Be sure to keep the walls of the container free of solid and adjust the aspirator suction so that the precipitate is always covered by a layer of liquid during this and all (but the last) successive washings. Then wash with (i) five 20 mL portions of glacial acetic acid; (ii) three 30 mL portions of absolute ethanol and (iii) six 15 mL portions of ether. Let the last batch of ether evaporate with about 30 seconds of suction and quickly transfer the product to a watch glass. Dry for about 25 minutes at 75 – 100 °C and transfer to a (previously weighed) tightly stoppered test tube or vial. Measure the EPR spectrum of your solid.

Prepare a solution of CuCl_2 using 1/10 the above amounts of Cu^{2+} , HCl , and water (**but no Na_2SO_3**). Compare the UV-visible spectrum of this (“blank”) solution to the solution you set aside before decanting. Use these spectra to estimate the amount of Cu(II) that is reduced to Cu(I) . Does this analysis agree with the yield of Cu(I) ? Be careful with your mass balance and discuss any qualitative difference in the two spectra.

Report (do not wait for the EPR results!)

Report the yield of product both in terms of the mass of the solid and the ratio of the UV-vis spectra. Write your report in the style of a Communication being sure to address the following: Write the balanced equation for the synthesis in this experiment. Why must the initial wash water contain HCl and Na_2SO_3 ? Why must the wash water always cover the precipitate? Using standard redox potentials, demonstrate the validity of the instability of Cu_{aq}^+ and calculate an upper limit for $[\text{Cu}_{\text{aq}}^+]$ in a solution containing 0.1M total copper (but no precipitating anions). CuCl dissolves in concentrated ammonia and in concentrated HCl . What species are formed? [Hint: what more common ion is isoelectronic with Cu(I)]. Do you expect your product to have an EPR spectrum? If your prediction were wrong, how would you explain it?

References:

W.L. Jolly, “Synthetic Inorganic Chemistry” Prentice Hall, Englewood Cliffs N.J. 1960, p 142.
R.W. Ramette and G. Fan, *Inorganic Chemistry*, **1983** 22, 3323.

E: Preparation of $[(\text{CH}_3\text{CH}_2)_2\text{NH}_2]_2[\text{CuCl}_4]$ Thermochromic Behavior of CuCl_4^{2-} Salts

When a substance changes color if heated beyond a certain temperature, the material is said to be thermochromic (thermo – heat, chromic – color). Thermochromism must arise because of change in the electronic structure (the bonding) of a material, but the electronic change can be driven by geometric changes of either the molecule or the solid lattice. There are two extreme types of thermochromic transitions: continuous and discontinuous. In a continuous transition, the color changes gradually over a large temperature range while in the discontinuous transition the color changes dramatically over a narrow temperature range.

The tetrachlorocuprate(II) anion is susceptible to thermochromism because it can undergo a change from square planar geometry to tetrahedral geometry. In the limit of D_{4h} geometry, d-d transitions of Cu^{2+} are symmetry forbidden (centrosymmetric as in O_h) and, hence, ϵ values are low. In contrast, in T_d geometry, the d-d transitions become more allowed, so the molar absorptivity increases considerably. Further, the crystal field splitting in D_{4h} complexes is similar to that found in O_h complexes and is larger than the crystal field splitting in T_d complexes. Thus, the energy of the d-d transition decreases when going from D_{4h} to T_d . Together, these effects account for the thermochromic behavior of CuCl_4^{2-} .

Alkylammonium salts of CuCl_4^{2-} are often thermochromic. It is thought that changing the temperature causes changes in the hydrogen-bonding of the cation. This, in turn, causes the geometry change of the transition metal anion complex, which resulting in the color change. Since moderate temperature changes only changes the total energy by a relatively small amount, it seems reasonable that a weak interaction such as hydrogen-bonding would be the underlying cause for the thermochromic transition.

Experimental

Dissolve about 0.01 mol of diethylammonium chloride (diethylamine hydrochloride) in 10 mL of isopropyl alcohol. Use gentle heating, if necessary. In a separate flask or test tube, dissolve 0.005 mol of anhydrous copper(II) chloride in 2 mL of absolute ethanol, again with gentle heating as necessary. Mix the two warm solutions and cool on an ice bath. After precipitation is complete, isolate the product by filtration and store in a desiccator. Measure the visible absorption spectrum (350–1100 nm) in aqueous solution and find the molar absorption coefficient for each peak. If there is a color change between the solid state and the aqueous solution, record the visible spectrum in a 1 M NaCl solution. Record the IR spectrum your salt at room temperature. To establish if (and where) the salt is thermochromic, use a melting point apparatus. Determine the temperature the color starts to change, the temperature the color change ends, and the melting point of the salt. Prepare thin films of the salt on two microscope slides, by rapid precipitation from a volatile solvent and test whether the thermochromicity is reversible (how fast?). If the salt is thermochromic (and nonreversible) below the melting temperature, measure the IR spectrum again for the high temperature isomer. Measure the solid state EPR spectra for samples prepared both above and below the thermochromic transition and compare them to the EPR spectrum of solid CuCl from Experiment D

Report

Write your report in the style of a Communication being sure to address the following: Include balanced chemical reactions for each synthetic step. Report the percent yield (be sure the sample is dry) and melting point of each salt. Be sure to use the IUPAC name of your product. Turn in all spectra. For the solution visible spectra, label each peak as CT or d-d and compare the λ_{max}

and ϵ for each salt. Are the copper complexes square planar or tetrahedral in solution? Show plots of visible spectra above and below the thermochromic transition on a single graph; Display the IR spectra above and below the thermochromic transition on a single graph; show an expanded view of the N-H stretching region above and below the thermochromic transition; indicate the temperature range of the thermochromic transition. Is the transition continuous or discontinuous? Is there evidence for a square planar to tetrahedral transition? If so, which structure corresponds to which temperature? Is there evidence of hydrogen-bonding changes associated with thermochromic transition? Why or why not? If so, which atoms are involved in the hydrogen-bonds?

Reference

S. Choi, J. A. Larrabee, *J. Chem. Ed.*, **1989**, 66, 774-776.

F: Preparation and Characterization of Metal Phthalocyanines

Phthalocyanine is an aromatic, planar, macrocyclic, tetradentate ligand that binds to nearly every metal on the Periodic Table. Metal phthalocyanines are highly colored substances that are sparingly soluble in most common solvents, so these compounds are frequently used as dyes and pigments. Metal phthalocyanines are normally synthesized by a template condensation of phthalonitrile (1,2 dicyanobenzene, see Shriver and Atkins p222). In the reaction, the metal ion holds the reacting phthalonitrile molecules in the correct geometry for ring closure to occur to form the metal phthalocyanine complex. Once the product is formed, it is remarkably stable with typical decomposition temperatures greater than 400 °C. In this exercise, a series of different metal phthalocyanine compounds will be prepared and their spectroscopic properties compared.

Experimental

For each metal salt assigned: add 1 mmol of the chloride (or chloride hydrate) salt to a round bottom flask. Flame-dry the flask with the metal salt in it until no more water vapors are driven off. After the flask has cooled to near room temperature, add 3 mmol of phthalonitrile and 3 mL of N,N-dimethylethanolamine. Add a dry reflux condenser containing a drying tube at the top and bring the mixture to reflux on a sand bath. After the reaction has turned deep blue, reflux an additional 10 min, then cool to room temperature. Add 10 mL of water, mix thoroughly, and filter. To the product, add 10 mL of methanol, mix thoroughly, and refilter. Measure the yield. Measure the IR spectrum of each product. Measure the visible (350-1100 nm) spectrum of each product in pyridine or N-methyl-2-pyrrolidinone; find the wavelength maxima and molar absorptivities of each peak. Take the ESR spectrum and describe it in terms of the electronic structure of your complex. Did you expect your complex to be diamagnetic? Is it?

Report

Write your report in the style of a Full Paper being sure to address the following: Write the balanced reaction for the synthesis of one of the metal phthalocyanine complexes. Report the percent yield for each reaction. Does the metal ion make a significant difference in reactivity? Why or why not? Compare the IR spectra of each compound. What vibrations are responsible for the major absorption peaks? What differences are there between the IR spectra of each compound? List the wavelength maxima and molar absorptivities for the visible spectrum for each compound. Assign the transitions in the visible spectrum as d-d, MLCT, LMCT, or ligand-ligand for each compound. What experimental evidence did you use to make these assignments? Turn in all spectra. Based on the molecular structure of the metal phthalocyanines, make a prediction about the solid state structure. Does this account for the poor solubility of this class of compounds? Why or why not? How does pyridine invoke solubility? In addition to your own written report, work with other students to create a class presentation which includes a discussion of the significance of phthalocyanines to chemistry, industry and biomedical science .

Reference

D. K. MacFarland, C. M. Hardin, M. J. Lowe, *J. Chem. Ed.*, **2000**, 77, 1484.