

Syllabus
CHM 402
Physical Inorganic Laboratory
Spring, 2007

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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 the references** given with each experiment is mandatory, as the handouts only give you enough information to get started on any experiment. Additional library work will be necessary for some experiments and should be fully cited in your reports. You **must** come into the laboratory each week prepared **prior** to starting the experiment and it is your responsibility to do so.

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 of **quality** similar to your CHM335 reports. 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. 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 the TA evaluation of your laboratory performance, preparation, and lab notebook.

Schedule: Section 1

Date	Jen	Kathryn	Ryan	Christina	Aby	Cole
January 24	Introduction to the Course					
January 31	A1	B	C1	E1	D	D
February 7	A2	C1	C2	E2	A1	E1
February 14	B	C2	D	D	A2	E2
February 21	C1	D	E1	A1	B	B
February 28	C2	E1	E2	A2	C1	A1
March 7	D	E2	A1	B	C2	A2
March 14	E1	A1	A2	C1	E1	C1
March 28	E2	A2	B	C2	E2	C2
April 4	F	F	F	F	F	F
April 11	F	F	F	F	F	F
April 18	F	F	F	F	F	F
April 25	Group Discussion of Project: Lab Cleanup, Checkout, All Reports Due					

Experiments:

A1: Preparation of $\text{K}_3\text{Cr}(\text{ox})_3 \cdot 3\text{H}_2\text{O}$.

A2: UV-Vis spectra of $\text{K}_3\text{Cr}(\text{ox})_3 \cdot 3\text{H}_2\text{O}$.

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

C1: Preparation and IR spectrum of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ isomer 1.

C2: Preparation and IR spectrum of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ isomer 2.

D: Preparation of Copper(I) Chloride

E1: Preparation of $[(\text{CH}_3\text{CH}_2)_2\text{NH}_2]_2[\text{CuCl}_4]$

E2: Spectroscopy of $[(\text{CH}_3\text{CH}_2)_2\text{NH}_2]_2[\text{CuCl}_4]$

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

**Products are to be turned in in labeled vials at the completion of each experiment.
Reports are due the lab period after completion of each experiment.**

Schedule: Section 2

Date	Jon	Jenna H	Jenna K	Grace	Amy	Ashley	Joe
January 26	Introduction to the Course						
February 2	A1	B	C1	D	D	B	D
February 9	A2	C1	C2	E1	A1	D	E1
February 16	B	C2	D	E2	A2	C1	E2
February 23	C1	D	E1	A1	B	C2	B
March 2	C2	E1	E2	A2	C1	A1	A1
March 9	D	E2	A1	B	C2	A2	A2
March 16	E1	A1	A2	C1	E1	E1	C1
March 30	E2	A2	B	C2	E2	E2	C2
April 6	F	F	F	F	F	F	F
April 13	F	F	F	F	F	F	F
April 20	F	F	F	F	F	F	F
April 27	Group Discussion of Project: Lab Cleanup, Checkout, All Reports Due						

Experiments:

A1: Preparation of $\text{K}_3\text{Cr}(\text{ox})_3 \cdot 3\text{H}_2\text{O}$.

A2: UV-Vis spectra of $\text{K}_3\text{Cr}(\text{ox})_3 \cdot 3\text{H}_2\text{O}$.

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

C1: Preparation and IR spectrum of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ isomer 1.

C2: Preparation and IR spectrum of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ isomer 2.

D: Preparation of Copper(I) Chloride

E1: Preparation of $[(\text{CH}_3\text{CH}_2)_2\text{NH}_2]_2[\text{CuCl}_4]$

E2: Spectroscopy of $[(\text{CH}_3\text{CH}_2)_2\text{NH}_2]_2[\text{CuCl}_4]$

F: Project – preparation and characterization of metal phthalocyanine complexes.

**Products are to be turned in in labeled vials at the completion of each experiment.
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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 easy to find for most of the electron configurations of octahedral complexes. 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 = $1/\lambda$).

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 in Chemistry*, Saunders, Philadelphia, **1977**, p. 411.

P. Atkins *et al*, *Shriver and Atkins Inorganic Chemistry*, 4th ed., W.H. Freeman, New York **2006**, chapter 19.

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.

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, especially 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).

Experimentally, IR spectra can be measured fairly readily on any type of material in any phase. Gas phase cells use long path lengths to achieve sufficient sample to observe spectra and are rather common. Liquids can be measured as thin films between two substrates. Liquid cells can be as simple as dabbing a drop of the sample between two NaCl plates to as complicated as elaborate gas tight cells needed to ensure stability of air-sensitive compounds. Solid samples are generally measured in one of two manners: as a finely ground mull or as a dilute mixture in an optically clear pellet. In the mull method the solid sample is finely ground in an agate mortar and pestle or by mechanical means (the powder must have particle sizes less than the wavelength of the IR light or else significant scattering problems occur) and then a drop or two of the mulling agent (Nujol, a high molecular weight hydrocarbon, or hexachlorobutadiene) are added to the sample and this mixture is further ground until a uniform slurry is formed. This is then added to a substrate plate like a liquid. If the absorption bands of the mulling agent do not overlap with the sample absorptions this method works well. The pellet methods do not suffer from interference problems if the solid mixing agent is chosen properly. A mixture of the sample and the "solvent" (about 1% w/w) are finely ground and put into a pellet maker and pressed at high pressure for 10-15 minutes until a clear pellet is formed. This pellet is then used to measure the IR spectrum. The choice of pellet material depends on the spectral region to be investigated: common materials are NaCl, good down to 600 cm^{-1} ; KBr, good down to 350 cm^{-1} ; and CsI, good down to 200 cm^{-1} . KBr is generally the medium of choice. CsI is hard to work with since it is quite soft and none of these materials is useful for wet samples. Also note that pellet formation is an exothermic process so that heat sensitive samples cannot be prepared in this manner.

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**.

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

In the ESR technique, we monitor the energy change as unpaired electrons “flip” from alignment *with* an applied magnetic field (B_0) to the opposite spin state. The transition is effected by microwave radiation and transitions are observed as absorption at a resonant frequency, ν , where (in the simplest case)

$$\Delta E = h\nu = g\mu_B B_0$$

Where μ_B is the Bohr magneton (we called it β in CHM401). The “g factor” is very close to 2 for a “free electron” (remember the formula for magnetic moment) but actually varies depending on the environment. In fact anisotropic complexes can have different g values for the three Cartesian directions

Splitting of the spin states occurs when the electron interacts with nearby atomic nuclear spins so that the simple (one line) spectrum indicated above, can become rather complicated even for a single unpaired electron. Results are usually reported as computed values of g and the distance (in gauss or millitesla) between the split lines.

In the actual ESR experiment, we keep ν constant and vary the magnetic field, B_0 . Transitions are usually displayed as the derivative of the absorption peak.

A good tutorial on EPR theory and some instrumental information can be found on the following website:

<http://www.bruker-biospin.com/brukerepr/continuouswavetheory.html>

Please be sure to work through the first several pages of this tutorial before we tackle an EPR analysis of your products. (note: on some browsers, Greek letters may not display accurately: e.g. eq 1.1 on the Bruker tutorial is $\Delta E = h\nu$)

Reference:

P. Atkins *et al*, *Shriver and Atkins Inorganic Chemistry*, 4th ed., W.H. Freeman, New York **2006**, pp181-183.

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 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?

Reference

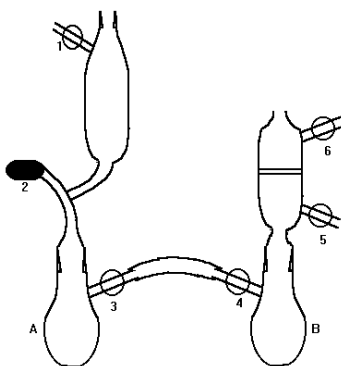
H. S. Booth, ed., "Inorganic Syntheses," McGraw-Hill, New York, **1939**, vol. 1, p. 37.

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 out balanced equations for the reactions that occurred and report the percent yield of the final product. Draw the structure of the product. Turn in the sealed vial of your product with your report.

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 as a KBr pellet. 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 $60\text{--}70^\circ\text{C}$ 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 and air dry 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. Measure the IR spectrum.

Report

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 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 will for about a minute and let it stand until the solid has settled to the bottom of the beaker. Carefully decant most of the liquid (into the waste bottle!) and 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. Determine the yield and measure its ESR spectrum.

Report (do not wait for the ESR spectrum!)

Write the balanced equation for the synthesis in this experiment. Report the yield of product. 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?

Reference:

W.L. Jolly, "Synthetic Inorganic Chemistry" Prentice Hall, Englewood Cliffs N.J. 1960, p 142.

E: Preparation of $[(\text{CH}_3\text{CH}_2\text{NH}_2)]_2[\text{CuCl}_4]$ 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 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 the ethylammonium chloride in 10 mL of isopropyl alcohol. Use gentle heating, if necessary. In a separate flask or test tube, dissolve 0.005 mol 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. Record the IR spectrum (KBr pellet) of each salt at room temperature. 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. 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 below the melting temperature, measure the IR spectrum both above and below the thermochromic transition. Measure the solid state EPR spectra above and below the thermochromic transition and compare them to the EPR spectrum of solid CuCl from Experiment D

Report

Write balanced chemical reactions for each synthetic step. Report the percent yield (be sure the sample is dry) and melting point of each salt. 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 as a KBr pellet. Measure the visible (350-1100 nm) spectrum of each product in pyridine; find the wavelength maxima and molar absorptivities of each peak.

Report

Write the balanced reaction for the synthesis of one of the metal phthalocyanine complexes. Report the per cent 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 and biomedical science .

Reference

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