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Laboratory Experiment

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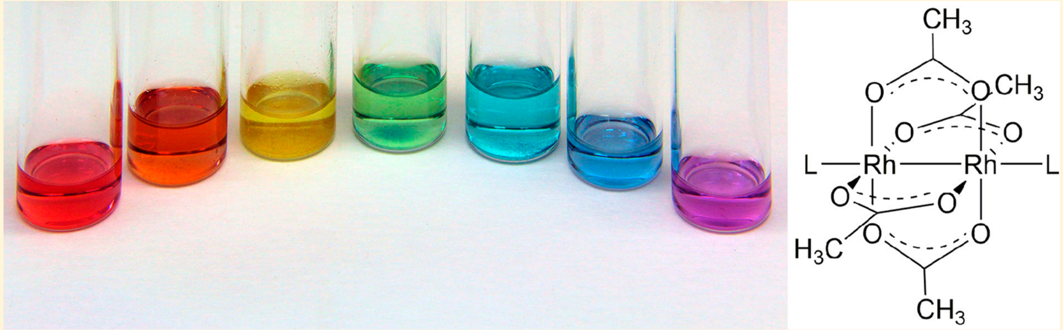
Rhodium Rainbow: A Colorful Laboratory Experiment Highlighting Ligand Field Effects of Dirhodium Tetraacetate

Evan Warzecha, Timothy C. Berto, Chad C. Wilkinson, and John F. Berry*

Department of Chemistry, University of Wisconsin, Madison, 1101 University Avenue, Madison, Wisconsin 53706, United States

Supporting Information



ABSTRACT: A new undergraduate inorganic chemistry laboratory experiment is presented. An introduction of the spectrochemical series and ligand exchange is explored using the coordination complex dirhodium tetraacetate, $Rh_2(OAc)_4$. Students have measured the absorption spectra of the Rh_2 complex in the presence of various ligand environments. In dichloromethane solution, $Rh_2(OAc)_4$ displays an absorption feature at 661 nm (222 M^{-1} cm^{-1}), which shifts to higher energy upon introduction of neutral axial ligands. The magnitude of the shift corresponds to the ligand's placement within the spectrochemical series. Experimental techniques of synthetic coordination chemistry and UV−vis spectroscopy are emphasized in this experiment as well as concepts such as molecular orbital (MO) diagrams and the spectrochemical series.

KEYWORDS: *Second-Year Undergraduate, Inorganic Chemistry, Hands-On Learning/Manipulatives, Spectroscopy, Coordination Compounds, Laboratory Instruction*

INTRODUCTION

The beautiful colors of coordination compounds are an attractive draw for students to study inorganic chemistry. These colors are a result of the electronic structures of metal complexes and, therefore, have been historically used as effective examples illustrating ligand field theory and molecular orbital theory as applied to transition metal compounds.[1−3] The effects of different ligands on the colors of transition metal compounds are summarized in the empirical "spectrochemical series" (Scheme 1), which is easily explained from a molecular orbital standpoint. Ligand field transitions most often involve electronic excitation from filled d orbitals of π symmetry to empty d orbitals of σ symmetry. Thus, π-donor and π-acceptor ligands modulate the energies of the π-symmetry donor orbitals upward and downward in energy, respectively. The π-donor ligands lead to lower-energy electronic transitions, and π-acceptor ligands give higher-energy electronic transitions; these two classes of ligands lie at extreme positions in the spectrochemical series.

Scheme 1. Spectrochemical Series

The Spectrochemical Series

increasing ligand field strength

$$\xrightarrow{\hspace{10em}}$$

π donor ligands	σ only ligands	π acceptor ligands
halides, thiocyanate, azide, hydroxide	water, ammonia, acetonitrile, pyridine	cyanide, phosphines, isonitriles, CO

The variation of ligand field as a function of ligand identity can lead to chromotropism and solvatochromism, in which reversible color changes occur depending on the nature of the solvent medium.[4] Given the vivid display of colors made possible by solvatochromic compounds, there are surprisingly few examples of this phenomenon that are suitable for an undergraduate inorganic chemistry laboratory course. In the course of our research on Rh_2 complexes,[5−10] we recognized that in the proper ligand environment the simple compound $Rh_2(OAc)_4$ is capable of displaying every one of the well-known hues of the visible color spectrum. The origin of the colors is readily interpretable with reference to the absorption

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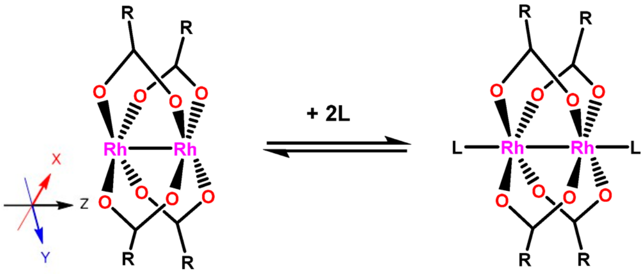
spectra and a molecular orbital description of the complexes. Thus, an undergraduate laboratory experiment highlighting these features, as presented here, provides a colorful venue for teaching aspects of synthetic chemistry, absorption spectroscopy, molecular orbital theory, metal−metal bonding, and solvatochromism. Though other laboratory experiments focusing on the spectrochemical series have been reported,[11−18] to our knowledge none of these experiments are capable of spanning the entire color spectrum.

Dirhodium tetracarboxylate "paddle wheel" complexes have important applications in a number of fields, including catalysis, medicinal chemistry, sensors, and phototherapeutics.[19−26] The first of these compounds to be synthesized in the 1960s was $Rh_2(O_2CH)_4(H_2O)_2$.[27] Since then, a wide array of analogues containing the dirhodium core surrounded by four carboxylato ligands have been prepared.[28] The most easily prepared example of this class of compounds is the $Rh_2(OAc)_4$ dimer used in this experiment.[29,30]

The general structure for a dirhodium carboxylato complex is shown in Scheme 2. Immediately of note in the structure are the two open coordination sites (one at each Rh center) along the Rh−Rh vector, the *z*-axis in Scheme 2. It is these sites that coordinate a variety of neutral ligands such as methanol, acetonitrile, pyridine, and others.[9,28,29] Anionic ligands bind as well.[28,29] The color of the resulting $Rh_2(OAc)_4(L)_2$ complex is highly dependent on the identity of the axial ligands, L, which is the main property investigated in this laboratory experiment.[29]

Scheme 2. Schematic Representation of $Rh_2(OAc)_4$ and the Corresponding Axially Coordinated Complex $Rh_2(OAc)_4(L)_2$[a]



[a] The provided coordinate system is intended to aid in understanding of the associated molecular orbitals.

The pedagogical goals of this experiment are the following:

- To allow the students to prepare an array of colorful compounds with a simple synthetic procedure
- To introduce the students to the concept of solvatochromism
- To train the students in the acquisition of UV−vis data
- To provide the students an opportunity to make connections between the colors of compounds and their optical spectra
- To challenge the students to interpret their optical spectra in molecular orbital terms, identifying the HOMO−LUMO gaps
- To illustrate an extension of molecular orbital concepts from the textbook cases of homonuclear diatomics to metal−metal bonded compounds that form σ, π, and δ bonding and antibonding combinations using d orbitals
- To guide the students to discover the spectrochemical series empirically
- To challenge the students to rationalize their spectrochemical series making use of π-donation and π-acid concepts

THEORETICAL BACKGROUND

Metal−metal bonds form via overlap of transition metal d orbitals. Within the 4-fold symmetric paddle wheel environment and the molecular coordinate system shown in Scheme 2, a metal−metal σ bond can form from the overlap of d_{z^2} orbitals, π bonds can be formed by overlap of d_{xz} and d_{yz} orbitals, and the overlap of two d_{xy} orbitals leads to a δ bond.[31−33] Just as the C−C π bond is weaker than a C−C σ bond in organic chemistry, the metal−metal π bonds are weaker than the σ bond, and the metal−metal δ bond is weaker still. Energetically, this means that the splitting between an in-phase σ bonding orbital and its out-of-phase σ* counterpart will be larger than the corresponding π−π* splitting, and δ−δ* splitting will be the smallest. The following energetic ordering of metal−metal bonding orbitals results (as shown in Figure 1): $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$. Each orbital can accommodate two valence electrons from the metal centers. The $Rh_2(OAc)_4$ formula indicates a Rh oxidation state of +2, which is a rare oxidation state for mononuclear Rh compounds, but allows for the formation of a Rh(II)−Rh(II) single bond by virtue of the 14 valence electrons (7 from each Rh(II) ion) filling the metal−metal bonding orbitals to give an overall $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ electron configuration.

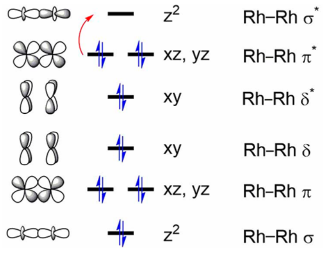


Figure 1. Molecular orbital diagram for a dirhodium "paddle wheel" complex such as $Rh_2(OAc)_4$. The red arrow indicates the electronic transition responsible for band A in the absorption spectrum.

Thus, the Rh−Rh single bond may be considered as an "electron rich" single bond due to the presence of all of the additional electron pairs that occupy the π, π*, δ, and δ* orbitals. It is instructive to make a bonding analogy to another important solvatochromic molecule in this respect: I_2. The I−I bond in I_2 is also an electron rich single bond, as I−I π and π* orbitals are all filled with additional electron pairs. In I_2, therefore, the unfilled I−I σ* orbital can act as an electron acceptor; donor solvent molecules can perturb the energy of this σ* orbital leading to a variety of different colors for I_2 in different solvents.[34,35] For example, solutions of I_2 in hexane or pentane, solvents with virtually no electron donating ability, are purple, just as I_2 is in the gas phase. In pyridine, however, I_2 turns red due to donation of the pyridine N lone pair of electrons into the I−I σ* orbital. The spectral changes are in part due to donor to I_2 charge transfer transitions, and partly due to the I_2 π* to σ* transition.[36] Because of its empty Rh−Rh σ* orbital, similar things happen with $Rh_2(OAc)_4$.

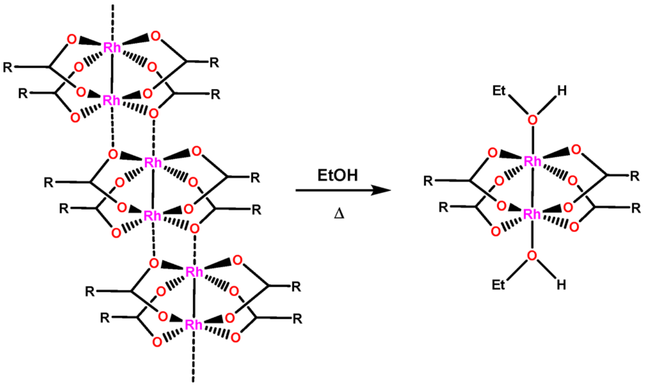
■ EXPERIMENTAL OVERVIEW

The rhodium rainbow experiment has been successfully run in five consecutive semesters of an intermediate-level inorganic chemistry course (CHEM 311), a course primarily targeted at students in their second year of undergraduate study. We had a total enrollment of 270 students spanning five semesters. This course often is the students' first introduction to in-depth analysis of spectra (i.e., using IR and UV−vis spectroscopies to infer molecular structure information), and one of the major goals of this experiment is to familiarize the students with UV−vis spectroscopy. This experiment is therefore coupled with an online UV−vis tutorial that the students perform as a prelab exercise. The information available to the students is given as Supporting Information for this paper. Our lab sessions run for 3 h, but this experiment takes roughly an hour; we therefore combine it with another short, but unrelated, experiment to fill the lab period.

Preparation of $Rh_2(OAc)_4(EtOH)_2$

Commercially available anhydrous $Rh_2(OAc)_4$ exists as an insoluble polymeric species. The polymer is "cracked" by reflux in ethanol ahead of time by the instructors. Students, working in pairs, are provided a sample of this solution at a concentration of 2 mg/mL (Scheme 3).

Scheme 3. Schematic Depiction of the Rhodium Acetate "Cracking" Process where Polymeric $[Rh_2(OAc)_4]_n$ Is Broken Down into Discrete Dimeric Units with the Structure $Rh_2(OAc)_4(EtOH)_2$



Absorption Spectra of $Rh_2(OAc)_4(L)_2$ Solutions

The students use aliquots of the rhodium dimer $Rh_2(OAc)_4$-$(EtOH)_2$ (2.0 mg/mL, EtOH) obtained as described above and add either neat liquids or solutions of exogenous ligands to obtain the entire spectrum of colors via exchange of the axial EtOH ligands. The quantities used to prepare the solutions are outlined in Table 1. To accommodate the small quantities used in this experiment, narrow-channel cuvettes with a 1.5 mL volume are utilized for obtaining the UV−vis spectra.

Recovery of the Rhodium

Although rhodium is an expensive element to employ in an undergraduate laboratory, this experiment is designed to be successful with small amounts of material. Over the course of five semesters, 270 students, working in pairs, have used ~1 g of $Rh_2(OAc)_4$. Furthermore, all rhodium species were efficiently collected for recovery by the laboratory instructors upon completion of the experiment.

In order to recycle the rhodium after one or more laboratory sessions, the solvents were removed from all rhodium solutions and the solid rhodium acetate adducts were dissolved in aqua regia and allowed to digest for 12 h. Distillation of the aqua regia resulted in a red solid. Extraction of this solid with concentrated HCl and recrystallization resulted in the formation of $RhCl_3 \cdot xH_2O$. $Rh_2(OAc)_4$ was then recovered by following a procedure adapted from that of Wilkinson and co-workers.[30] The above preparation of $Rh_2(OAc)_4(EtOH)_2$ can then, once again, be performed. To test the purity, the $Rh(OAc)_4(EtOH)_2$ dimer was precipitated by reducing the volume of the solution by half and cooling the solution, which resulted in the formation of a blue/dark green crystalline material, which was collected by vacuum filtration. Purity is established by FT-IR or ^1H NMR spectroscopy (see Supporting Information, Figures S1 and S2).

■ HAZARDS

Proper protective equipment such as gloves, goggles, and a lab coat should be worn during this experiment. Rhodium acetate is a known toxin, and care should be taken not to inhale or touch the compound with exposed skin; toxicity data for the complexes do not exist, so they should be assumed to be as toxic as rhodium acetate. Ethanol is flammable and toxic when ingested or inhaled. Dichloromethane is a known irritant, and the vapors may cause dizziness. Acetonitrile is a lachrymator and a potential irritant. Pyridine is both flammable and toxic when ingested, inhaled, or absorbed through the skin. It gives off an unpleasant fishy odor. In general, all solvents should be handled in properly functioning fume hoods and should be capped before removal from the hood. Triphenylphosphine is toxic when ingested and may cause sensitization of the skin. In addition, it is extremely toxic to aquatic organisms and should thus only be disposed of via proper avenues. Recovery of the rhodium requires the use of both aqua regia and 12 M HCl and is meant only to be performed by the course instructors or other experienced personnel.

Table 1. Quantities Used in the Preparation of Various $Rh_2(OAc)_4(L)_2$ Complexes

Ligand (L)	$Rh_2(OAc)_4(EtOH)_2$ (2.0 mg/mL, EtOH) (mL)	Ligand Solution Volume (mL)	EtOH (mL)	Total Volume (mL)	Color
Ethanol (neat)	0.625		0.625	1.25	Blue
Acetonitrile (neat)	0.625	0.625	0	1.25	Violet
Sodium isonicotinate (2.0 mg/mL, aq)	0.625	0.625	0	1.25	Red
Benzaldehyde (neat)	0.625	0.625	0	1.25	Green
Toluenesulfonylmethyl isocyanide (TosMIC) (2.0 mg/mL, CH_2Cl_2)	0.625	0.625	0	1.25	Yellow
Triphenylphosphine (PPh_3) (1.0 mg/mL, CH_2Cl_2)	0.125	0.50	0.50	1.125	Orange

■ RESULTS AND DISCUSSION

Synthetic Chemistry

In contrast to the kinetically inert equatorial acetate ligands, the axial EtOH ligands in $Rh_2(OAc)_4(EtOH)_2$ are labile and easily displaced by other axial ligands. The students accomplish this by adding new ligands, either neat or in solution, to a solution of $Rh_2(OAc)_4(EtOH)_2$ in ethanol solution of $Rh_2(OAc)_4(EtOH)_2$ in EtOH. Using a broad set of ligands that span the spectrochemical series, the students attain all hues of the visible spectrum. Figure 2 shows a "Rhodium Rainbow" students prepared using the axial ligands described in Table 1. Table S1 provides a catalogue of other ligands that we have tested, arranged by color, with some technical notes. See Figure S3 for an example of an expanded rainbow prepared with some of these additional ligands. The UV−vis spectrum of each solution is measured as soon as possible after it is prepared in order to minimize solvent evaporation and precipitation of the PPh_3 compound.

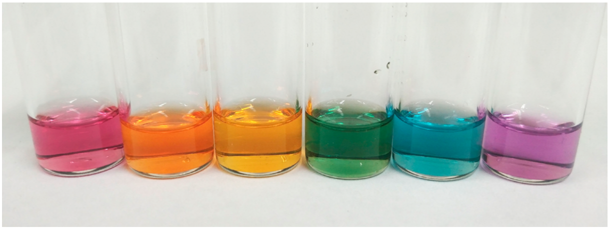


Figure 2. $Rh_2(OAc)_4$ solutions with various axial ligands. From left to right: sodium isonicotinate, PPh_3, *p*-toluenesulfonylmethyl isocyanide, benzaldehyde, ethanol, acetonitrile.

Absorption Spectra of $Rh_2(OAc)_4(L)_2$

Directly after the laboratory experiment, the students are asked to analyze their UV−vis spectra to determine the HOMO−LUMO energy for each compound and to produce an ordering of the ligands from smallest to largest HOMO−LUMO energy: i.e., a spectrochemical series. Notably, in our course, this spectrochemical series is derived empirically before ligand field theory is introduced in the lecture. After the students are introduced to ligand field theory, they are asked to revisit the data from this lab to derive a deeper understanding of the colors of $Rh_2(OAc)_4$ adducts. Here, their visible absorption spectra are analyzed with reference to the molecular orbital diagram for metal−metal bonding given in Figure 1. Absorption spectra of dirhodium tetracarboxylate complexes show two major features: The lowest-energy transition is sensitive to the nature of axial ligands. A second band appears at ~450 nm, is insensitive to axial ligation, and mainly involves the Rh−O bonds to the equatorial carboxylate ligands.[28] Figure 3 shows an overlay of absorption spectra for $Rh_2(OAc)_4(L)_2$ obtained by students with the six ligands described above.

The assignment of the lowest-energy transition caused some disagreement in early literature reports, but the available data are consistent with the assignment of this band as being due to an electronic transition within the Rh_2 core of dirhodium carboxylato complexes.[37,38] More specifically, the transition occurs between the occupied Rh_2 π^* orbital, the HOMO of the compound, and the unoccupied Rh_2 σ^* LUMO as shown in the MO diagram provided in Figure 1. Ligand coordination to the axial sites on $Rh_2(OAc)_4$ is thus able to perturb either the Rh_2 π^* or σ^* orbitals involved in the HOMO−LUMO transition. For example, coordination of an axial π-donating ligand is expected to destabilize the Rh_2 π^* and σ^* orbitals and thus decrease the HOMO−LUMO gap as compared to a pure σ-donor ligand that only interacts with the σ^* orbital, causing the lowest-energy transition to occur at lower energy and longer wavelengths for the π-donor complex.

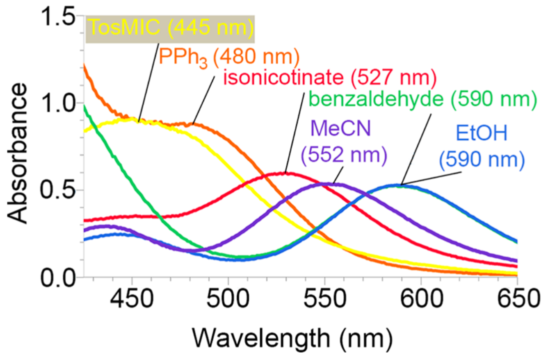


Figure 3. Absorption spectra of $Rh_2(OAc)_4(L)_2$ where L = isonicotinate, PPh_3, *p*-toluenesulfonylmethyl isocyanide, benzaldehyde, ethanol, acetonitrile. The lowest-energy band can be seen to shift to higher energy (lower wavelength) in accordance with the spectrochemical series.

In this laboratory experiment, the students determine the HOMO−LUMO transition energies from their spectra and correlate the identity of the axial ligand (L) in $Rh_2(OAc)_4(L)_2$ and the observed absorption maximum $\lambda(\max)$. From these data, the students are asked to order the ligands according to the HOMO−LUMO energies that they obtain, thus deriving empirically a spectrochemical series. After ligand field theory is introduced to the students in the lecture, they are asked to revisit their data from this laboratory experiment and to analyze it in molecular orbital terms in a postlab follow-up assignment.

Assessment of the Pedagogic Goals for the Experiment

With regard to the pedagogic goals listed in the Introduction, we may comment on the efficacy of a few of them on the basis of the qualitative observations of an experienced teaching assistant, comments from students on a moderated student forum, and analysis of student responses. Primarily, we aimed for a high degree of reproducibility in the experimental procedure. The procedure described here is streamlined to the extent that we can report no failures, except when students inadvertently mix the wrong reagents. In our course, this experiment serves as the first for the students to use UV−vis spectrometers. Standard practices in UV−vis spectroscopy, such as reaching a target absorbance, are introduced and emphasized. The students additionally take an online UV−vis tutorial as a prelab exercise. The students obtain very consistent data during this experiment. The large majority of students report $\lambda(\max)$ values for the HOMO−LUMO transitions in these compounds within ±3 nm of the instructor's reference spectra, with occasional differences within ±10 nm.

One of the major goals is to get students to identify the HOMO−LUMO transitions for these compounds, and ~80−90% of our students are able to do so. There are two factors that make it difficult for some students to properly identify the HOMO−LUMO transition. First, some students try to assign the most intense transition in the spectrum as the HOMO−

LUMO transition rather than the lowest-energy transition. Second, the HOMO−LUMO transitions for the PPh_3 and TOSMIC solutions sometimes appear as a shoulder on a higher-energy band in the UV, which causes the students to have some difficulty in picking out this transition.

The final initial goal for the experiment is for the students to derive a spectrochemical series from the ligands given, and in our course they do this before ligand field theory has been presented in the lecture. The students who are able to correctly derive the HOMO−LUMO energies are invariably able to derive the spectrochemical ordering of the ligands correctly. After ligand field theory has been introduced in our lecture, the students are asked to address the deeper intellectual goal of rationalizing the spectrochemical series in molecular orbital terms. This goal is met with more limited success; about 50% of our students have difficulty connecting the empirical spectrochemical series to a molecular orbital picture. The concept of metal−ligand π bonding is the major hurdle here, which will be an area of further development for the supporting materials for this experiment as well as the lecture component of the class.

■ SUMMARY

A laboratory experiment focused on connecting the concepts of absorption spectroscopy, the spectrochemical series, and ligand substitution is presented that is suitable for an undergraduate inorganic chemistry course. The experiment also provides an introduction to second row transition metal chemistry and is one of very few undergraduate experiments in the literature that utilize rhodium, an element that features prominently in inorganic chemistry textbooks, and one that has extremely important applications in catalysis. The presented experiment is also versatile within the inorganic curriculum and has been used to emphasize concepts such as MO diagrams, metal−metal bonding interactions, ligand substitution, absorption spectroscopy, inorganic synthesis, and solvatochromism.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00648.

> Example procedure, instructor's notes, UV−vis tutorial exercise, as well as the IR spectrum of $Rh_2(OAc)_4(EtOH)_2$ and the NMR spectrum of $Rh_2(OAc)_4$ (PDF, DOCX)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: berry@chem.wisc.edu.

ORCID

Evan Warzecha: 0000-0001-7007-9250

John F. Berry: 0000-0002-6805-0640

Notes

The authors declare no competing financial interest.

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