

Simultaneous Introduction of Redox and Coordination Chemistry Concepts in a Single Laboratory Experiment

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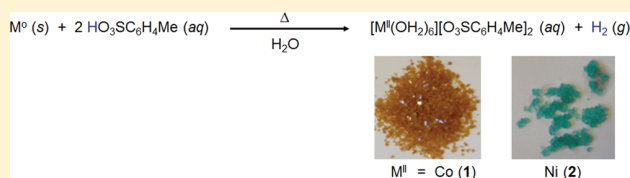
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S Supporting Information

ABSTRACT: The preparation of two crystalline binary transition metal *p*-toluenesulfonate salts of $[M^{II}(\text{OH}_2)_6][\text{OTs}]_2$ stoichiometry, where $M^{II} = \text{Co}$ (1) and Ni (2), is described. Their syntheses are accomplished via an oxidation–reduction reaction using metal powders and aqueous *p*-toluenesulfonic acid hydrate as the reducing and oxidizing reagents, respectively. Over the span of one 4 h session, students learn concepts that include reaction stoichiometry, relative rates, complexation, crystal growth and isolation, and fractional crystallization methods. A second session allows for the origins of color and spectroscopy (UV–vis and infrared) to be investigated by more advanced students. Suitably equipped laboratories may also pursue independent student projects involving additional microscopy, X-ray solution and refinement, and magnetic susceptibility exercises.

KEYWORDS: Laboratory Instruction, Hands-On Learning/Manipulatives, High School/Introductory Chemistry, First-Year Undergraduate/General, Upper-Division Undergraduate, Inorganic Chemistry, Inquiry-Based/Discovery Learning, Aqueous Solution Chemistry, Coordination Compounds, Crystal Field/Ligand Field Theory



INTRODUCTION

Oxidation–reduction reactions are important but poorly understood concepts that are relevant to many biological, chemical, and materials science issues.^{1–6} Particularly daunting chemical reactions for high school and undergraduate students are those involving oxidation–reduction as multiple abstract concepts such as stoichiometry, electron transfer, oxidation states, and metathesis are often simultaneously involved.^{4–6} Consequently, oxidation–reduction reactions have received considerable attention from chemical educators in an effort to better understand and develop the cognitive theory and strategies for understanding chemical reactions.^{7–11}

According to Johnstone, chemical knowledge requires an understanding of three general concepts: macroscopic, submicroscopic, and symbolic.^{7–9} In this context, macroscopic observables follow chemical reaction progress by the senses (i.e., color change, heat or gas evolution, evaporation, combustion, etc.), while submicroscopic aspects are more abstract as interactions of individual molecules, ions, or particles remain unseen. The third and probably the most difficult stage of learning is the comprehension of the symbolic representations and jargon associated with chemical equations. In general terms, learning breaks down when relationships between these components are neglected or worse, omitted altogether. It follows that student proficiency requires mastery

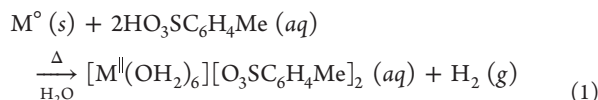
of all three concepts and may be encouraged via directed hands-on discovery exercises.^{7–11}

Preparative inorganic chemistry often relies on the conversion of reactive transition metal complexes containing weakly coordinating anions such as perchlorate, tetrafluoroborate, and hexafluorophosphate. Unfortunately ClO_4^- anions are strongly oxidizing, and BF_4^- and PF_6^- can undergo hydrolysis to produce HF in aqueous solution;¹² trifluoromethanesulfonate (triflate) salts tend to be rather expensive. Like their triflate counterparts, structurally related and less expensive binary transition metal *p*-toluenesulfonate salts are known for a variety of transition metal,^{13–20} lanthanide,²¹ and alkali metal ions²² but have received little attention as precursors in inorganic synthetic transformations. The primary advantages of these salts are that they (1) are nonoxidizing, (2) do not undergo aqueous hydrolysis, and (3) have lower solubility than many other weakly coordinating anions in polar solvents (e.g., MeOH, H_2O , and DMF).^{16–18,23,24} The general synthesis of hexaaqua transition metal *p*-toluenesulfonates is as follows:

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In this experiment, aqueous oxidation of transition metal powders with *p*-toluenesulfonic acid readily forms crystalline octahedral complexes of $[M^{\text{II}}(OH_2)_6][OTs]_2$ stoichiometry ($M^{\text{II}} = \text{Co}$, 1; Ni , 2), where OTs^- is an outer sphere and charge balancing *p*-toluenesulfonate anion (eq 1). Crystallization techniques, crystal morphology, and physical origins of color (eyeball and UV–vis spectroscopy) in two transition metal complexes may also be explored in a single cost-effective and time efficient experiment. Advanced students may also explore magnetic susceptibility,²⁵ X-ray diffraction concepts,²⁶ structural determinations and techniques,^{27–29} and crystal morphology studies²⁶ as independent projects in the following inquiry-based experiment.

EXPERIMENTAL PROCEDURES

Materials

Large-scale preparations of $[Co(OH_2)_6][OTs]_2$ (1) and $[Ni(OH_2)_6][OTs]_2$ (2) and their infrared spectra have been previously described.¹⁹ Solid *p*-toluenesulfonic acid hydrate (Acros), cobalt and nickel metal powders (Strem, –325 mesh), and deionized (or distilled) water were used as received.

Equipment

The experiment requires glassware common to most teaching laboratories. The necessary reagents are inexpensive and maintain their usability for several months to years when stored free from water vapor. Solutions containing reaction products are air and water stable for several weeks, and their isolation may be accomplished in two 4 h laboratory periods.

Synthesis of $[Co(OH_2)_6][OTs]_2$ (1): Part 1

Solid *p*-toluenesulfonic acid (1.002 g, 5.273 mmol) and cobalt powder (0.617 g, 1.05 mmol) were combined as solids and placed into a beaker containing water (8 mL). The mixture was heated in a hot water bath (90 °C) for 90 min, during which time the color gradually changed from gray to pink. The reaction mixture was filtered while warm through a pipet/Kimwipe filter combination into a 50 mL beaker. The filtrate beaker was covered with a watch glass and allowed to crystallize at room temperature overnight. The orange crystals were removed from the mother liquor via spatula and placed onto a dry filter paper for 15 min. Typical yield: 0.45 g (31%). UV–vis (H_2O): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_M/M^{-1} \text{ cm}^{-1}$) 475 (3.6; ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$), 512 (4.7; ${}^4T_{2g}(P) \leftarrow {}^4T_{1g}(P)$). $\mu_{\text{eff}}(\mu_B) = 3.9$.

Synthesis of $[Ni(OH_2)_6][OTs]_2$ (2): Part 1

Solid *p*-toluenesulfonic acid (1.000 g, 5.262 mmol) and nickel powder (0.615 g, 1.05 mmol) were combined as solids and placed into a test tube containing water (7 mL). The mixture was heated in a hot water bath (90 °C) for 90 min, during which time the color gradually changed from gray to pale green. The reaction mixture was filtered while warm through a pipet/Kimwipe filter combination into a 50 mL beaker. The filtrate beaker was covered with a watch glass and allowed to crystallize at room temperature overnight. The green crystals were removed from the mother liquor via spatula and placed onto a dry filter paper for 15 min. Typical yield: 0.75 g (52%). UV–vis (H_2O): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_M/M^{-1} \text{ cm}^{-1}$) 393 (4.5; ${}^3T_{1g} \leftarrow {}^3A_{2g}$), 659 (1.8; ${}^1E_g \leftarrow {}^3A_{2g}$), 721 (4.3; ${}^3T_{1g} \leftarrow {}^3A_{2g}$). $\mu_{\text{eff}}(\mu_B) = 2.8$.

Characterization of Complexes: Part 2

UV–vis data for 1 and 2 were collected as aqueous solutions in the 250–850 nm range and molar extinction coefficients were calculated for each absorption.^{30–32} Assignments were made using Tanabe-Sugano diagrams and the data agreed with previous reports for octahedral hexaaqua cobalt(II) and nickel(II) complexes.^{33–38} Infrared spectra for 1 and 2 were obtained as Nujol mulls between KBr plates and were compared to starting materials. Assignments were made for the observed infrared absorptions.^{19,39,40} As independent projects, students with more advanced skills and instrumentation access may also study crystal morphology²⁶ using microscopes and pursue single-crystal structural determinations^{27–29} using a local diffractometer or electronically available data sets.^{14,15} Room-temperature magnetic characterization of solid samples was performed on a Johnson-Matthey magnetic susceptibility balance using previously described methods.²⁵

HAZARDS

Students are required to wear safety glasses, gloves, and laboratory coats during the experiment. Solid *p*-toluenesulfonic acid hydrate [CAS 6192–52–5] is a hygroscopic and corrosive solid. Cobalt [CAS 7440–02–0] and nickel [CAS 7440–48–4] metal powders are inhalation hazards, and finer mesh sizes (i.e., less than –325 mesh) are not advisable. Each solid should be handled with care to minimize skin contact. Solutions containing *p*-toluenesulfonic acid are acidic and disposable gloves should be worn at all times. In the event of skin exposure, the affected area should be washed with cold water, followed by solid sodium bicarbonate, and repeated washing with cold water. Students are provided with material data safety sheets for all reagents and are quizzed about potential hazards and safety considerations before the experiment begins.

RESULTS AND DISCUSSION

This experiment has been performed over the past nine years in a senior level inorganic chemistry laboratory course with 5–25 enrolled students working either as individuals or in pairs, for small and large classes, respectively. In this course, students routinely prepare and isolate their complexes, collect and interpret UV–vis and infrared spectra, and obtain magnetic susceptibility data (Supporting Information, S4–S16). Students have also mounted crystals onto an X-ray goniometer head and solved their structures using freely available data refinement and solution software as part of their independent study projects for the past six years.^{27–29} Given that crystals of the aqua complexes are often twinned, a second module was developed where coordinated water is replaced by dimethylfomamide ligands. Single-crystal X-ray solution and refinement exercises in a senior inorganic laboratory are less cumbersome with these anhydrous crystals (Supporting Information, S17–S25). For advanced students, additional experimental techniques, instructions, and technical report grading rubric may also be found in the Supporting Information (S26–S32). A third experiment module was also developed in an effort to introduce crystallization techniques and the origins of color to high school and general chemistry students; this final experiment has been successfully completed on three separate occasions (Supporting Information, S33–S38).

Reaction progress may be monitored by following the color of the mixture and remaining metal powder. With increasing reaction time, the color intensity grows and allows for a crude

estimation of reaction trajectory to be visually monitored as formation of highly colored and soluble $[M^{II}(\text{OH}_2)_6][\text{OTs}]_2$ ($M^{II} = \text{Co}$, **1**; Ni , **2**) coordination complexes occur. In both reactions, the initially colorless mixtures gradually change to orange or green with concomitant disappearance of metal powder for **1** and **2**, respectively. During the two electron oxidation–reduction (hydrogen displacement) reactions, zerovalent transition metal powders are transformed into divalent hexa(aqua) complexes via reduction of acidic protons (in blue) from *p*-toluenesulfonic acid (eq 1). For safety considerations, *p*-toluenesulfonic acid is present in substoichiometric quantities to minimize the risk of crystalline product contamination (by acid) and manipulation of corrosive aqueous solutions. Additionally, slow evolution of dihydrogen during the reaction proceeds at a sufficiently slow rate rendering fume hood use unnecessary for the synthesis of **1** and **2** while electric stirrer hot plates are used.¹⁹

Fractional crystallization is a commonly used technique for the separation and purification of materials. In this experiment, crystallization and microscopy are used to differentiate crystals of **1** and **2** from their starting materials. Despite being a limiting reagent, *p*-toluenesulfonic acid hydrate may remain in reaction mixtures as slow oxidation of the metal powders occurs. The desired metal-containing salts are separated from the parent acid by fractional crystallization due to solubility differences in aqueous solution. Given that aqueous *p*-toluenesulfonic acid is more soluble than either **1** or **2**, the less soluble complexes are easily crystallized upon cooling. Moreover, crystals of **1** and **2** are highly colored, while the acid hydrate is colorless, which allows for visual and microscopic confirmation of these intrinsic properties. The oxidation and spin states of the Co^{II} ($S = 3/2$) and Ni^{II} ($S = 1$) centers may also be deduced via bulk magnetic susceptibility on a Johnson-Matthey Magnetic Susceptibility balance using the procedure described by Girolami.²⁵

Crystal morphology has been used for the identification of simple binary salts and crystal forms produced by different polymorphs of the same material. With the use of polarizer–analyzer microscope attachments, it can be shown that a given crystal may be either single or contain a “twin”. Through use of an optical polarizer, a chosen crystal can be shown to be one of these cases as extinctions of cross-polarized light at every 90° rotation position will change reproducibly for a single crystal; aggregates or twins will show more complicated behavior.²⁶ We note that large and highly colored crystals of **1** and **2** readily form upon slow evaporation and allow detailed investigations of their crystallization properties to be explored under low- and higher-power magnifications (Figures 1 and 2).^{14,15,18,19,26} Crystalline plates of **2** also display several commonly encountered defects such as inclusions, aggregation and step growths features.²⁶

Electronic Spectra Analysis

The apparent colors of **1** and **2** are related to the energy of absorbed visible light and are reflective of general periodic trends expected for octahedral transition metal complexes (Irving-Williams series).^{30–32,35–37,41–45} Aqueous solutions of **1** (orange) and **2** (green) exhibit different solution colors suggesting that the absorption energies or complementary colors of their electronic transitions are red–green and orange–blue, respectively. Given that the Pauling scale electronegativities of zerovalent cobalt and nickel (1.88 and 1.91), it is reasonable to assume that divalent complexes will

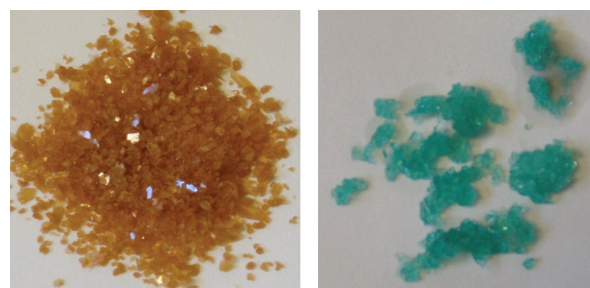


Figure 1. Crystalline samples of (left) **1** and (right) **2**.

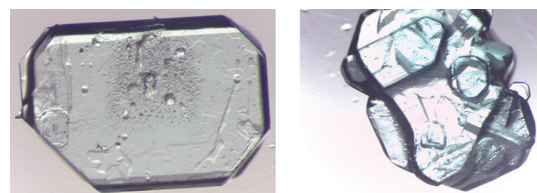


Figure 2. (left) Microscope image of a single crystal of **2**. Bubbles and striations are the result of air trapped in the crystallographic oil used (Paratone-N). (right) A crystal aggregate of **2**.

also display color differences in their solid and solution states.^{30–32}

Colors of materials are representative of the types and allowed nature of the electronic transitions present.^{35–37,41–49} Aqueous solutions of **1** and **2** contain octahedral $[M^{II}(\text{OH}_2)_6]^{2+}$ cations in addition to outer sphere charge-balancing *p*-toluenesulfonate anions, whose optical transitions occur in the ultraviolet region of the electromagnetic spectrum. The remaining transitions for the salts lie in the visible region and belong to absorptions within the 3*d* orbital manifold. The electronic absorptions have weak intensities owing to the spin-allowed and Laporte forbidden nature of the transitions between the nonbonding t_{2g} and weakly antibonding e_g orbital sets.^{36,38,42,47,49} Given that metal-to-ligand (or ligand-to-metal) charge transfer absorptions are absent in spectra of **1** and **2**, the optical appearance of their solutions is directly related to the energy and selection rules associated with their *d*-*d* transitions (Table 1).^{38,46,49,50}

Table 1. Absorption and Transmission of Light Relationships

Absorbed Light Color	Absorbed Light (λ , nm)	Transmitted Light Color	Transmitted Light (λ , nm)
Red	650	Green	520
Orange	600	Blue	450
Yellow	580	Dark Blue	430
Yellow–green	570	Violet	410
Blue–green	490	Red	620
Blue	450	Yellow	600
Violet	400	Yellow–green	560

In an Irving-Williams hard/soft frame, the energies of the optical absorptions are expected to shift as a function of divalent transition metal for a given common ligand set:



Provided that these are also roughly proportional to the hydration enthalpy of the metal coordination sphere for

borderline metal ions,³⁰ ionic radii [89 and 83 pm] and charge density considerations predict **2** will display a larger Δ_o parameter in comparison to **1**, given that $\text{Co}^{\text{II}}_{\text{HS}}$ is more electropositive and has a larger ionic radius than Ni^{II} . In a purely electrostatic crystal-field splitting model, the magnitude of Δ_o should also be greater for **2** as the Ni^{II} center has a smaller ionic radius and higher effective nuclear charge (Z_{eff}).^{36,37,43,46,49,51} However, from a molecular orbital standpoint, only sigma bonding interactions are present in octahedral $[\text{M}^{\text{II}}(\text{OH}_2)_6]^{2+}$ complexes with the strongest ones found for the hexa(aqua)nickel(II) ion, owing to efficient overlap of the oxygen atom orbitals with the more electronegative and radially contracted Ni^{II} orbitals.^{30–32,35–37,45,46,51–53} Consequently, a larger octahedral splitting parameter (Δ_o) is expected for the Ni^{II} analogue, ignoring the influence of weak Jahn–Teller effects in the Co^{II} case.^{31,32,35,36} Consistent with these assumptions, literature reports show the Δ_o values for $[\text{Co}^{\text{II}}(\text{OH}_2)_6]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{OH}_2)_6]^{2+}$ are considerably different and are 9750 and 8500 cm^{-1} [1026 and 1176 nm] for **1** and **2**, respectively.^{39,52,37} Given the appearance of the UV–vis spectra obtained for aqueous solutions of **1** and **2**, we conclude that octahedral ions are present.^{34,40,43,48}

For more advanced students (i.e., chemistry majors), the optical absorption spectra may be further investigated further to estimate the magnitude of their octahedral splitting (Δ_o) and Racah (B) parameters.^{42–47,49} In **2**, the absorption maxima may be used to estimate both Δ_o and B in the frame of the spectrochemical series, considering spin-allowed transitions of the d^8 $[\text{Ni}^{\text{II}}(\text{OH}_2)_6]^{2+}$ ions:^{33,35,36,38,50}

$$\nu_1 \quad {}^3T_{2g} \leftarrow {}^3A_{2g} \quad 8500 \text{ cm}^{-1} (1026 \text{ nm})$$

$$\nu_2 \quad {}^3T_{1g}({}^3F), {}^1E_g \leftarrow {}^3A_{2g} \quad 13,500 \text{ cm}^{-1} (741 \text{ nm})$$

$$\nu_3 \quad {}^3T_{1g}({}^3P) \leftarrow {}^3A_{2g} \quad 25,300 \text{ cm}^{-1} (395 \text{ nm})$$

where the energy difference between the ${}^3A_{2g}$ and ${}^3T_{2g}$ states gives $\Delta_o = 1026 \text{ nm}$ for **2**. However, only visible range absorptions are responsible for the apparent color and are largely dependent on the energies of ν_2 and ν_3 . The complementary color (Table 1) of these necessarily leads to the apparent color (green) of **2**. In other words, a minimum in the absorption intensity at about 500 nm gives the green color of **2**.^{33,35–38,43,50}

In comparison, understanding the orange appearance of **1** is more complicated, owing to the presence of multiple electronic transitions in the visible region. Given that **1** contains d^7 $[\text{Co}^{\text{II}}_{\text{HS}}(\text{OH}_2)_6]^{2+}$ ions, the relevant spin-allowed optical transitions are^{33–38,43,47,50,51}

$$\nu_1 \quad {}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F) \quad 8350 \text{ cm}^{-1} (1198 \text{ nm})$$

$$\nu_2 \quad {}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F) \quad 16,000 \text{ cm}^{-1} (625 \text{ nm})$$

$$\nu_3 \quad {}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F) \quad 19,400 \text{ cm}^{-1} (515 \text{ nm})$$

The ${}^4T_{1g}$ ground state can participate in three light-induced excitations to afford quartet states [${}^4T_{2g}$, ${}^4T_{1g}$, ${}^4T_{1g}$] arising from there are three spin-allowed optical transitions from the ${}^4T_{1g}(F)$ ground state. The lowest energy one (ν_1) lies in the near-infrared region and is outside the experimental range transitions from the ground state ${}^4T_{1g}(F)$ have three spin-allowed transitions of ${}^4T_{2g}$, ${}^4A_{2g}$, and ${}^4P_1(P)$ symmetry, while the lowest energy one [${}^4T_2 \leftarrow {}^4T_1$] occurs in the near-infrared and

is outside the experimental range. The other two overlap in the visible region of the spectrum with the ν_2 absorption dominating the ν_3 (shoulder) one. These factors ultimately lead the orange appearance of **1**.^{33–38,43,47,50,51}

The experimental learning outcomes are

- Learn microscale inorganic synthetic techniques (crystallization, filtration) with product yield and appearance used for assessment.
- Develop a better understanding of spectroscopic characterization techniques (UV–vis). Interpretation of spectra using Tanabe–Sugano diagrams reinforces color concepts and their origins in $3d$ complexes. Data manipulation using Excel and other graphing programs will also improve data analysis skills.
- Practice infrared spectra interpretation and make assignments using chemical literature. These exercises will encourage a better understanding of molecular and electronic structures in organic and inorganic complexes.
- Allow introductions to crystallographic concepts (defects, morphology) using microscopy. Advanced undergraduates may also pursue single-crystal X-ray solution and refinement as independent projects.

CONCLUSIONS

We have described an experiment that offers many opportunities for inquiry-based learning. The laboratory experiment links several concepts such as reaction chemistry, symmetry, and electronic structure using inexpensive and commonly available solid reagents and equipment. The preparation of the two crystalline and air- and water-stable salts enables various redox and coordination chemistry concepts to be investigated during the course of the introductory experiment. Students are required to master microscale crystallization and filtration techniques during the isolation of their crystalline solids.

The synthetic and crystallization portions of the experiment were successfully conducted by high school students and teachers and adapted to include chemistry undergraduates and advanced independent projects. The experiment may be performed without dedicated lectures and is easily modified considering student aptitudes, facilities, and time constraints. We note the experiment uses water as a reaction solvent and air-sensitive techniques and equipment are not required.

The experiment also introduces more advanced concepts appropriate for senior undergraduate students where a deeper understanding of interrelationships between period trends, color, spin-only magnetism, symmetry, and electronic transitions are appropriate. These independent activities include coordination chemistry, origins of color, infrared and electronic spectroscopy, crystal morphology, and single-crystal X-ray diffraction (solution and refinement) concepts and methods. The experiments culminate in written reports where comparisons of student data to literature and related compounds are described. These activities have been successfully implemented in an advanced inorganic laboratory and practiced over the past six years.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00256.

Additional experimental information (Student and Instructor instructions, Pascal's constants) and technical grading rubric information (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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