

# Coordination Compounds: Chemistry and Application

## Introduction

Coordination compounds are metal ions surrounded by ligands. Ligands are either anions or molecules that can donate electrons into the d-orbitals of the metal ion and form a bond. Examples of common ligands are chloride ion, cyanide ion, ammonia, ethylenediamine, and ethylenediaminetetraacetate ion (EDTA). The metal ions that form coordination compounds are from a group of metals known as transition metals. These metals have more than one oxidation state. This property allows the transition metals to act as Lewis acids.

Coordination chemistry plays an important role in the purification of metals. Many metals are not found in the pure state in nature. For example, gold ore can be treated with cyanides to form  $[\text{Au}(\text{CN})_2]^-$  which is soluble in water. Impurities remain behind and after treatment with zinc, pure gold is obtained. Pure nickel and silver are also isolated by first converting the metal into coordination compounds. The formation of insoluble coordination compounds aids in the determination of the amount of metal present in a mixture. Distinctively colored coordination compounds that form with various metals can be used to identify the presence of a metal in a mixture. For example, iron may be identified by the formation of a reddish coordination compound with potassium thiocyanate (remember qualitative analysis experiment in chem. 201).

Ethylenediaminetetraacetate (EDTA), shown in Fig. 1, is very effective in forming a water-soluble coordination compound with lead. This process can be used to treat lead poisoning.

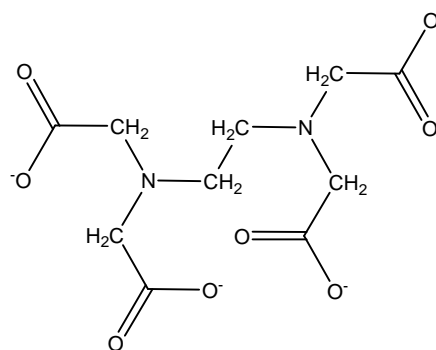
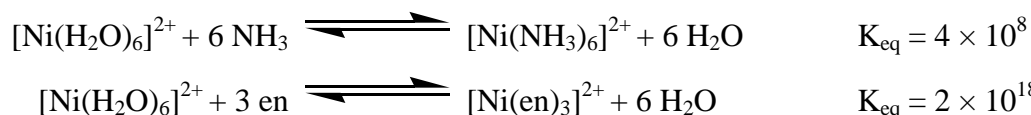


Fig. 1  $\text{EDTA}^{4-}$   
(ethylenediaminetetraacetate ion)

## Chemical Foundations

**Donor Atom** The donor atom is the atom of the ligand that binds to the metal ion. If one donor atom is present, as in ammonia, the ligand is referred to as **monodentate**. If two donor atoms are present, as in ethylenediamine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ), the ligand is **bidentate**. If more than two donor atoms are present, the ligand is **polydentate**. EDTA is a polydentate ligand because it contains six donor atoms (see Fig. 2). If  $\text{EDTA}^{4-}$  combines with  $\text{Ca}^{2+}$ , the resulting complex is  $[\text{Ca}(\text{EDTA})]^{2-}$ . Bidentate and polydentate ligands have a much greater affinity for binding than monodentate ligands even with the same donor atom due to entropic differences (i.e., less overall entropy is lost upon the binding of a smaller number of molecules with the same number of water molecules released). For example, ethylenediamine forms a complex with  $\text{Ni}^{2+}$  more readily than ammonia:



**Chelating Agent** The word “chelate” is derived from a Greek word meaning “claw”. Ligands are referred to chelating agents because they surround and hold the metal ion like a claw.

**Coordination Number** The coordination number refers to the number of atoms in a ligand bonded to the metal ion. The most common coordination numbers are 4 and 6. In the case of the

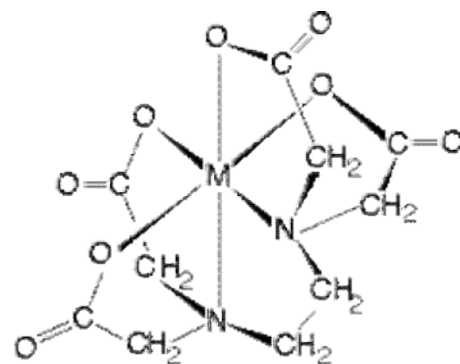


Fig. 2 Metal-EDTA complex

tetramminecopper(II),  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , there are four nitrogen atoms from the  $\text{NH}_3$  molecules each bonded to  $\text{Cu}^{2+}$ . Hexachloroplatinate(IV),  $[\text{PtCl}_6]^{2-}$ , is an example of an anion with a coordination number of six.

**Oxidation Numbers of Coordination Complexes** The net charge on the coordination complex results from the difference between the charge of the metal ion and the anion. For example,  $[\text{PtCl}_6]^{2-}$  is a complex ion formed from one  $\text{Pt}^{4+}$  and six  $\text{Cl}^-$ , which results in a net charge of 2-. In a case where the ligand does not carry a formal charge, such as  $\text{NH}_3$ , an ammonia complex carries the charge of the metal ion, for example  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  has a charge of 2+, which is the oxidation number of copper.

**Geometry of Coordination Compounds** Coordination compounds with a coordination number of 2 are linear. If the coordination number is 4, the coordination complex is either square planar or tetrahedral. When the coordination number is 6, the complex is octahedral. See *Appendix A* for the geometries of coordination compounds.

**Crystal Field Theory** Crystal field theory assumes that the interaction between the metal ion and the ligand is electrostatic. The ligands are able to split the energies of the transition metal  $d$  orbitals into lower and higher energy states (Fig. 3). Visible light will excite an electron from a lower energy  $d$  orbital to a higher energy  $d$  orbital. This accounts for many of the properties of coordination compounds, such as color and magnetic properties. The color of coordination compounds depends on both the metal and the ligand. Ligands can be arranged in order of their increasing energy gap between the lower and higher energy  $d$  orbitals; this arrangement of the ligands is known as the spectrochemical series.

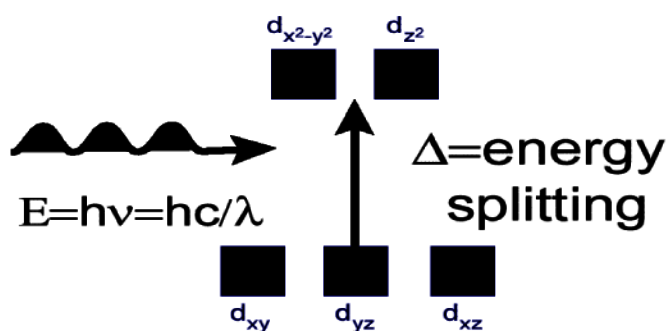


Fig. 3 d-orbital splitting in an octahedral structure

In a tetrahedral structure, the splitting energy ( $\Delta_o$ ) is smaller than that of the octahedral structure (as there are only four ligands as compared to six ligands in the octahedral). Furthermore, the splitting is reversed, i.e. the  $d_{xy}$ ,  $d_{yx}$ , and  $d_{xz}$  orbitals are higher in energy than the  $d_{x^2-y^2}$  and  $d_{z^2}$ .

**Spectrochemical Series** Based on data for a wide variety of complexes, it is possible to list ligands in order of increasing field strength (i.e. splitting energy,  $\Delta_o$ ) in the spectrochemical series as follows:

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^- < \text{F}^- < \text{urea} < \text{OH}^- < \text{ox} < \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{pyridine} < \text{NH}_3 < \text{ethylenediamine} < \text{NO}_2^- < \text{CH}_3^- < \text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}$ .

It is possible to arrange the metals according to a spectrochemical series as well. The approximate order is:

$\text{Mn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{V}^{2+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{V}^{3+} < \text{Co}^{3+} < \text{Mn}^{3+} < \text{Mo}^{3+} < \text{Rh}^{3+} < \text{Ru}^{3+} < \text{Pd}^{4+} < \text{Ir}^{3+} < \text{Pt}^{4+}$

## Demonstration

### Observations of Nickel (II) Coordination Compounds with Various Ligands

Several different ligands will be added to beakers containing a 0.1 M solution of  $\text{Ni}^{2+}$  ions. Answer the following questions based on your observations of the demonstration.

1. What changes are observed if the following reagents are added to the  $\text{Ni}^{2+}$  solution slowly with stirring? Record the observed color and associated  $\lambda_{\text{max}}$  in the absorption spectra when:
  - a. no ligand is added
  - b. ammonia is added
  - c. 25% ethylenediamine is added
  - d. 50% ethylenediamine is added
  - e. 75% ethylenediamine is added

(A table may help organize your observations.)

2. Based on the data obtained for Question 1, rank the ligands in a series from weakest field ligand to strongest. Are your observations in line with what you would expect based on the spectrochemical series? How does the amount/concentration of the ligand influence the changes?
3. Draw the expected octahedral structure for each of the complexes in Question 1 a-e.

# Experiment

## Ligand Coordination of Transition Metal Ions

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### Introduction

This lab will explore several aspects of coordination compounds and crystal field theory. The colors of many transition metal complexes can be explained by crystal field theory. The  $d$  orbitals of an isolated metal ion all have the same energy. When ligands bind to a metal ion in a particular configuration (e.g., octahedral, tetrahedral, square planer; see *Appendix A*), the orientation of the metal ligand bond relative to the different  $d$  orbitals splits the orbitals according to their energy levels. The magnitude of the difference in energy between the  $d$  orbitals varies depending on the metal ion and the nature of the ligands. Electrons in the lower  $d$  orbitals can be promoted to a higher energy orbital with the absorption of the appropriate wavelength of light according to the equation  $E = hc/\lambda$ . If the  $d$  orbitals are empty or full ( $d^0$ ,  $d^{10}$ ), then no electron can be promoted between the orbitals; hence, these ions are often colorless (e.g.,  $\text{Cd}^{2+}$ ). The higher the energy difference between the  $d$  orbitals, the shorter the wavelength of light then corresponds to the energy absorbed.

The color visually observed is the result of the subtraction of the absorbed color from the remainder of the spectrum. The following table describes how the observed color relates to a complementary absorbed color (i.e., wavelength of light).

Table 1 Relation between colors of observed and absorbed light

Observed Color	Absorbed Color	Absorbed Wavelength (nm)
Green-Yellow	<u>Violet</u>	400
Yellow	<u>Blue</u>	450
Red	<u>Blue-Green</u>	490
Violet	<u>Yellow-Green</u>	570
Dark Blue	<u>Yellow</u>	580
Blue	<u>Orange</u>	600
Green	<u>Red</u>	650

Name: \_\_\_\_\_, Class: CHEM 203, Section: \_\_\_\_\_  
Semester: \_\_\_\_\_

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### Pre-Laboratory Questions

1. How many electrons are in the  $d$  orbitals of the following metal ions:  $V^{2+}$ ,  $Co^{4+}$  and  $Fe^{3+}$ ?

Ion	# d-Electrons
$V^{2+}$	
$Co^{4+}$	
$Fe^{3+}$	

2. Assume an octahedral geometry for both complexes, draw the following: (Use your chemistry textbook as a reference to answer this question.)

a) the low-spin electron configuration for a complex containing  $Mn^{2+}$

b) the high-spin electron configuration for a complex containing  $Fe^{2+}$ .

3. The absorbance maxima observed for the following cobalt complexes ( $[Co(NH_3)_6]^{3+}$   $\lambda_{max} = 470$  nm,  $[Co(NH_3)_5Cl]^{2+}$   $\lambda_{max} = 560$  nm,  $[Co(NH_3)_4Cl_2]^+$   $\lambda_{max} = 630$  nm, and  $[Co(NH_3)_3Cl_3]$   $\lambda_{max} = 680$  nm) can be identified with transitions involving  $d$ -electrons.

a) Should the spectrochemical series apply for these complexes? Why or why not? (HINT: Think of the criteria needed for these complexes to be fairly compared.)

b) Is the trend in wavelength the same as you would predict using the spectrochemical series? Hint: Take this problem step-by-step.

## Experimental Procedure, Data & Observations

You will use a well plate to mix various ligands (structures shown in *Appendix B*) with several different metal ions to produce the complexes shown below. (See *Appendix C* for a template that can be placed under the well plate as a guide):

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Ti}(\text{EDTA})]^-$	$[\text{TiCl}_4]^-$			
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Ni}(\text{EDTA})]^{2-}$	$[\text{NiCl}_4]^{2-}$	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	$[\text{Ni}(\text{en})_3]^{2+}$	$[\text{Ni}(\text{im})_6]^{2+}$
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Co}(\text{EDTA})]^{2-}$	$[\text{CoCl}_4]^{2-}$		$[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$	$[\text{Ni}(\text{im})_4(\text{H}_2\text{O})_2]^{2+}$
$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Zn}(\text{EDTA})]^{2-}$			$[\text{Ni}(\text{en})_1(\text{H}_2\text{O})_4]^{2+}$	$[\text{Ni}(\text{im})_2(\text{H}_2\text{O})_4]^{2+}$

### Part A: Spectrophotometer Calibration

Follow the procedure in *handout given to you by your Professor* to calibrate the Ocean Optics spectrophotometer. Use water as a blank sample for zeroing the spectrophotometer. Set the wavelength range from 425 to 700 nm.

Handle all cuvettes by the rim, and wipe the outside of the cuvette with a dry paper towel before placing into the spectrophotometer.

### Part B: $\text{Ti}^{3+}$ ion complexes

Place 0.5 mL of 0.1 M  $\text{Ti}_2(\text{SO}_4)_3$  into 3 wells of a well-plate. Then add the designated amounts of reagent or water to the corresponding well. Make a visual observation and determine the absorbed wavelength by transferring each solution to a cuvette and placing each into the spectrophotometer.

Well Num.	Reagent	mL of Reagent	mL of Water	Complex Ion	Observed Color	$\lambda_{\text{max}}$	Long $\lambda_{\text{max}}$	$\Delta_o$ kJ/mol
A1		-	1.5	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$				
A2	0.1 M EDTA	1.5	-	$[\text{Ti}(\text{EDTA})]^-$				
A3	Satd. NaCl	1.5	-	$[\text{TiCl}_4]^-$				

### Part C: Ni<sup>2+</sup> ion complexes

Put 0.5 mL of a 0.1 M Ni(NO<sub>3</sub>)<sub>2</sub> solution into 10 wells of a well plate. In a hood, add the amounts of reagent and/or water to the corresponding well then individually make a visual observation and determine the  $\lambda_{\max}$ . Use the longest wavelength peak (**Long  $\lambda_{\max}$** ) to determine the splitting energy  $\Delta_o$  in kJ/mol. (Remember, from Chem 201, that  $E_{\text{photon}} = h\nu$ ).

Well Num.	Reagent	mL of Reagent	mL of Water	Complex Ion	Observed Color	$\lambda_{\max}$	Long $\lambda_{\max}$	$\Delta_o$ kJ/mol
B1		-	1.5	[Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>				
B2	0.1 M EDTA	1.5	-	[Ni(EDTA)] <sup>2-</sup>				
B3	Satd. NaCl	1.5	-	[NiCl <sub>4</sub> ] <sup>2-</sup>				
B4	0.3 mL aq. NH <sub>3</sub>	1.5	-	[Ni(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>				
B5	0.1 M en	1.5	-	[Ni(en) <sub>3</sub> ] <sup>2+</sup>				
C5	0.1 M en	1.0	0.5	[Ni(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>				
D5	0.1 M en	0.5	1.0	[Ni(en) <sub>1</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>				
B6	0.2 M im	1.5	-	[Ni(im) <sub>6</sub> ] <sup>2+</sup>				
C6	0.2 M im	1.0	0.5	[Ni(im) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>				
D6	0.2 M im	0.5	1.0	[Ni(im) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>				

Note: en = ethylenediamine; im = imidazole

### Part D: Co<sup>2+</sup> ion complexes

Add the designated amounts of reagent or water to 3 wells containing 0.5 mL 0.1 M aq. CoSO<sub>4</sub> and make a visual observation in addition to recording  $\lambda_{\max}$ .

Well Num.	Reagent	mL of Reagent	mL of Water	Complex Ion	Observed Color	$\lambda_{\max}$	Long $\lambda_{\max}$	$\Delta_o$ kJ/mol
C1		-	1.5	[Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>				
C2	0.1 M EDTA	1.5	-	[Co(EDTA)] <sup>2-</sup>				
C3	Satd. NaCl	1.5	-	[CoCl <sub>4</sub> ] <sup>2-</sup>				

### Part E: $\text{Zn}^{2+}$ ion complexes

Put 0.5 mL of a 0.1 M  $\text{ZnSO}_4$  solution into 2 wells of a well plate. Add the amounts of reagent or water to the corresponding well and make a visual observation.

Well Num.	Reagent	mL of Reagent	mL of Water	Complex Ion	Observed Color
D1		-	1.5	$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$	
D2	0.1 M EDTA	1.5	-	$[\text{Zn}(\text{EDTA})]^{2-}$	

### Conclusions and Discussion

1. Draw the low-spin electron configurations for  $\text{Ti}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ .

2. For the nickel ion series involving water and ligands containing nitrogen donor atoms, address the following questions:

a. Based on the corresponding  $\lambda_{\text{max}}$ , do the ligands, ammonia, ethylenediamine, and water, follow the spectrochemical series? Explain.

b. Imidazole is another ligand containing nitrogen donor atoms. Based on your results, where does imidazole lie in the spectrochemical series relative to ammonia, ethylenediamine and water?



- c. EDTA contains both nitrogen and oxygen donor atoms. Where does EDTA lie in the spectrochemical series in relation to the amine-containing ligands and water?
- d. Arrange nickel complexes in the order of increasing  $\Delta_o$ , and compare between this arrangement and the spectrochemical series.
3. The comparison of the chloride complex to the other complexes for a given metal ion series in this experiment is not properly explained by the spectrochemical series. Why?
4. Describe your observations for the zinc ion complexes and explain the results.
5. Rank  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Ti}^{3+}$  with regard to the metal ion spectrochemical series. Use the EDTA ligand complexes for your comparison.

## References

1. [www.uncp.edu/home/mcclurem/courses/chm226/introduction\\_Coordination\\_Chemistry.pdf](http://www.uncp.edu/home/mcclurem/courses/chm226/introduction_Coordination_Chemistry.pdf)
2. [www.public.asu.edu/~jpbirk/CHM-115\\_BLB/ClassNotes/chpt24.pdf](http://www.public.asu.edu/~jpbirk/CHM-115_BLB/ClassNotes/chpt24.pdf)
3. [www.unine.ch/chim/chw/Chapter4.html](http://www.unine.ch/chim/chw/Chapter4.html)
4. Inorganic Chemistry, Gary Wulfsberg, University Science Books Pub., 2000, p 370-393
5. “Universal Spectrochemical Series of six-coordinate Octahedral Metal Complexes for Modifying the Ligand Splitting”, Tomohiko Ishii, Shino Tsuboi, Genta Sakane, Masahiro Yamashita and Brian K. Breedlove, Dalton Transactions, 2009, 680-687
6. Spectral Characteristics of the Copper(III) and Nickel(III) Coordination Compounds with Open-Chain Macrocyclic dioxotetraamines, Polyhedron, Volume 19, Issues 26-27, 2000, p 2533-2538

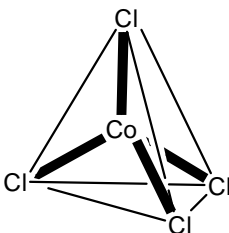
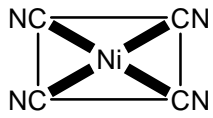
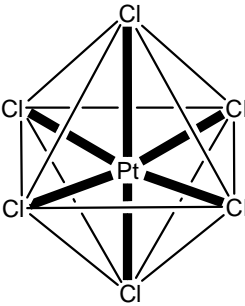
## Appendix A

### Geometries of Coordination Compounds

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A compound's geometry (i.e., how the ligands are arranged around the metal atom) determines its physical and chemical properties. For example, a tetrahedral compound will behave differently than a square planar compound that contains the same metal atom and the same ligands.

Consider the complex ion,  $[\text{CoCl}_4]^{2-}$ . Its coordination number is equal to 4; thus, the structure of  $[\text{CoCl}_4]^{2-}$  might be tetrahedral or square planar (see examples). Experimentally,  $[\text{CoCl}_4]^{2-}$  has been shown to have a tetrahedral structure. Linear and octahedral are the most common geometries for coordination numbers 2 and 6, respectively.

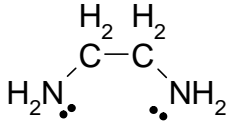
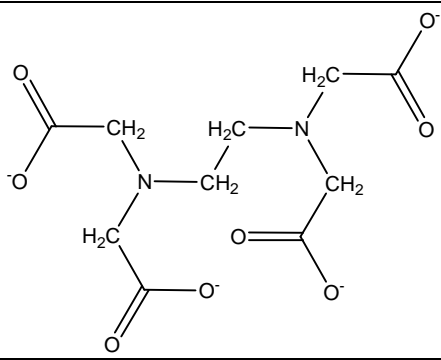
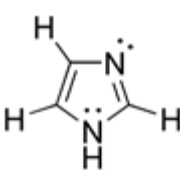
<i>Example</i>	<i>Sketch</i>
$[\text{CoCl}_4]^{2-}$ <u>tetrahedral</u> CN = 4 ligands attached at the corners of a tetrahedron	
$[\text{Ni}(\text{CN})_4]^{2-}$ <u>square planar</u> CN = 4 ligands attached at the corners of a square	
$[\text{Ag}(\text{NH}_3)_2]^+$ <u>linear</u> CN = 2 ligands and metal atom connected in a straight line	$\text{H}_3\text{N} \text{---} \text{Ag} \text{---} \text{NH}_3$
$[\text{PtCl}_6]^{2-}$ <u>octahedral</u> CN = 6 ligands attached at the corners of a octahedron	

## Appendix B

### Structures of Selected Ligands

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Structures for some of the ligands that will be used in this experiment are shown below.

<i>Ligand</i>	<i>Structure</i>
Ethylenediamine (en)	 <chem>NCCN</chem>
Ethylenediaminetetraacetate ion (EDTA <sup>4-</sup> )	 <chem>[O-]C(=O)CN(CC(=O)[O-])CCN(CC(=O)[O-])CC(=O)[O-]</chem>
Imidazole (im)	 <chem>C1=CN=CN1</chem>

## Appendix C

### Well Microtiter Plate Template

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If you are using a 24 well plate, place your plate on a copy of this sheet to assist with the layout in your plate. However, if you are using a 48 well plate, draw your own chart similar to the one in this appendix, and place the indicated solutions in every other well.

Numbers in the cells represents the amount (in mL) of each reagent to add.

- “M” represents the metal ion, which in most cases is stated at the left of the row. **Note:** *Four cells in the lower right corner of the well plate will contain Ni<sup>2+</sup> solutions despite the metal ion label on the left of that row.*
- “L” represents the ligand stated at the top of the column.
- “W” represents water to add in addition to the ligand stated at the top of the column.

	H <sub>2</sub> O	EDTA	Cl <sup>-</sup>	NH <sub>3</sub>	en	im
Ti <sup>3+</sup>	M: 0.5 L: 1.5	M: 0.5 L: 1.5	M: 0.5 L: 1.5			
Ni <sup>2+</sup>	M: 0.5 L: 1.5	M: 0.5 L: 1.5	M: 0.5 L: 1.5	M: 0.5 L: 1.5	M: 0.5 L: 1.5	M: 0.5 L: 1.5
Co <sup>2+</sup>	M: 0.5 L: 1.5	M: 0.5 L: 1.5	M: 0.5 L: 1.5		Ni <sup>2+</sup> : 0.5 L: 1.0 W: 0.5	Ni <sup>2+</sup> : 0.5 L: 1.0 W: 0.5
Zn <sup>2+</sup>	M: 0.5 L: 1.5	M: 0.5 L: 1.5			Ni <sup>2+</sup> : 0.5 L: 0.5 W: 1.0	Ni <sup>2+</sup> : 0.5 L: 0.5 W: 1.0

# Instructions for Laboratory Assistant

## Reagents:

4 X 100 mL 0.1M  $\text{Ti}_3(\text{SO}_4)_2$   
4 X 100 mL 0.1  $\text{Ni}(\text{NO}_3)_2$   
4 X 100 mL 0.1  $\text{CoSO}_4$   
4 X 100 mL 0.1  $\text{ZnSO}_4$   
4 X 100 mL 0.1  $\text{Na}_2\text{EDTA}$   
4 X 100 mL 0.1 Sat'd  $\text{NaCl}$   
4 X 100 mL 0.1 M Ethylenediamine (en)  
4 X 100 0.2 M Imidazole

## Supplies:

16 4 X 6 well plates

## Also needed for demo:

1 small dropper bottle 100% ethylenediamine

## Equipment (in room)

disposable pipets  
cuvettes  
ocean optics spectrophotometers

**Students will wear gloves for this experiment. All sizes should be available.**