

VISIBLE ABSORPTION SPECTROSCOPY OF COBALT COMPLEXES

Introduction

When many cobalt(II) salts are dissolved in water, the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion is formed, which has an octahedral geometry and is pale-pink in color. Addition of HCl to $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ results in the formation of blue $[\text{CoCl}_4]^{2-}$, which has a tetrahedral geometry. Similarly, addition of KSCN to $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ results in the formation of violet $[\text{Co}(\text{SCN})_4]^{2-}$, which also has a tetrahedral geometry.

The color of transition metal complexes can be explained by **ligand field theory**. According to this theory, the degeneracy of the d-orbitals is removed in the presence of a ligand field. In the case of an octahedral ligand field, three of the d-orbitals are lowered in energy and form the t_{2g} orbitals, whereas the remaining two are raised in energy and form the e_g orbitals. Transition metal complexes appear colored because the splitting of the d-orbitals matches the energy of certain wavelengths of visible light. As white light passes through a colored solution, certain wavelengths of light are **subtracted** from the spectrum. The color of the solution is the **complimentary color** to the color of light absorbed by the solution. Since red and green are complimentary colors, a solution which absorbs red light appears green in color and a solution which absorbs green light appears red in color.

Absorbed Color	Approximate Wavelength	Observed Color	Approximate Wavelength
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-Green	490	Red	620
Yellow-Green	570	Violet	410
Yellow	580	Dark Blue	430
Orange	600	Blue	450
Red	650	Green	520

Suppose light of some wavelength λ and some initial intensity I_0 passes through a solution which absorbs light of that wavelength. Some light will be absorbed by the solution and the rest will be passed through with reduced intensity I . A quantity known as **percent transmittance** is defined as follows.

$$\text{Percent transmittance } (\%T) = (I/I_0) \times 100$$

This is closely related to a quantity known as **absorbance**, which is defined according to the following equation.

$$\text{Absorbance} = 2 - \log (\%T)$$

You should be able to see from these equations that the percent transmittance for a colorless solution would be 100%, and therefore the absorbance would be zero. Similarly, if a solution is so intensely colored that no light passes through the solution, the percent transmittance would be 0% and the absorbance would be 2. If the absorbance of a solution is measured at many different wavelengths, the result is an **absorption spectrum**, which shows which wavelengths of light are absorbed by a solution.

The absorbance is related to a number of properties. The first is the **path length** of the cell. The longer the path length of the cell, the greater will be the reduction in the intensity of the light. You may have noticed that the color of water in a pool looks more intense in the deep end of the pool than in the shallow end; this is essentially the same phenomenon. A second factor that influences absorbance is the **concentration** of the solution. An increase in concentration results in a corresponding increase in absorbance. These terms are combined into the following equation, which is known as the **Beer-Lambert law**.

$$A = \epsilon lc$$

In this equation, **l** represents the path length of the cell, **c** represents the concentration of the cell, and **ϵ** is the **molar absorptivity constant** for the compound, which is a unique constant for a particular compound at a particular wavelength. This constant is a measure of **how strongly** a compound absorbs at a particular wavelength. Since path lengths are usually measure in cm, the units associated with the molar absorptivity constant are $\text{lit mol}^{-1}\text{cm}^{-1}$.

As noted previously, the colors of transition metal complexes arise from a splitting of the d-orbitals in the presence of attached ligands. When the energy difference between the orbitals matches the energy of incoming light, light is absorbed by the solution and energy is used to promote an electron from one of the lower-energy t_{2g} orbitals to one of the higher-energy e_g orbitals. Several quantum mechanical selection rules govern the frequency with which such absorptions can occur. One such rule states that electronic transitions cannot occur in molecules which posses a center of symmetry. Since octahedral complexes possess a center of symmetry, the electronic transitions are said to be **spin-forbidden**. Some transitions do occur, however, due to vibrations that relax the symmetry of the molecule. Tetrahedral complexes, in contrast, lack a center of symmetry. Electron transitions are not spin-forbidden, and the colors of the corresponding complexes are more intense. The color of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is rather pale in contrast to the color of $[\text{CoCl}_4]^{2-}$ because a change in geometry from octahedral to tetrahedral occurs.

In this laboratory, your goal is to measure the absorption spectra of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$. You will determine the wavelength at which each complex absorbs most strongly, and calculate the molar absorptivity of each compound at that wavelength.

PROCEDURE

1. Obtain a 10 mL graduated cylinder and three tubes for use with the spectrometer. Do not use ordinary test tubes with the spectrometer.
2. Fill the first tube with deionized water. This tube will be used to zero the instrument. Fill the second tube with 0.10 M CoCl_2 .
3. To the 10 mL graduated cylinder add 1 mL of 0.010 M CoCl_2 . Carefully pipette 4 mL of 12 M HCl into the graduated cylinder so that the total volume is 5 mL. Fill the third spectrophotometer tube with this solution, and **seal the top with a small square of parafilm** to avoid exposing the spectrometer to HCl vapors. Be sure that the exterior of each tube is dry.

It is not necessary to completely fill the spectrometer tubes. In fact, each tube need only be roughly one-third full.

We will be using Thermo Scientific Genesys 20 spectrometers to make the absorbance measurements. A diagram of a spectrometer is shown on the shown on the following page.

4. To make an absorbance measurement, follow the following steps:

[a] Open the sample compartment door and load the first tube (containing water).

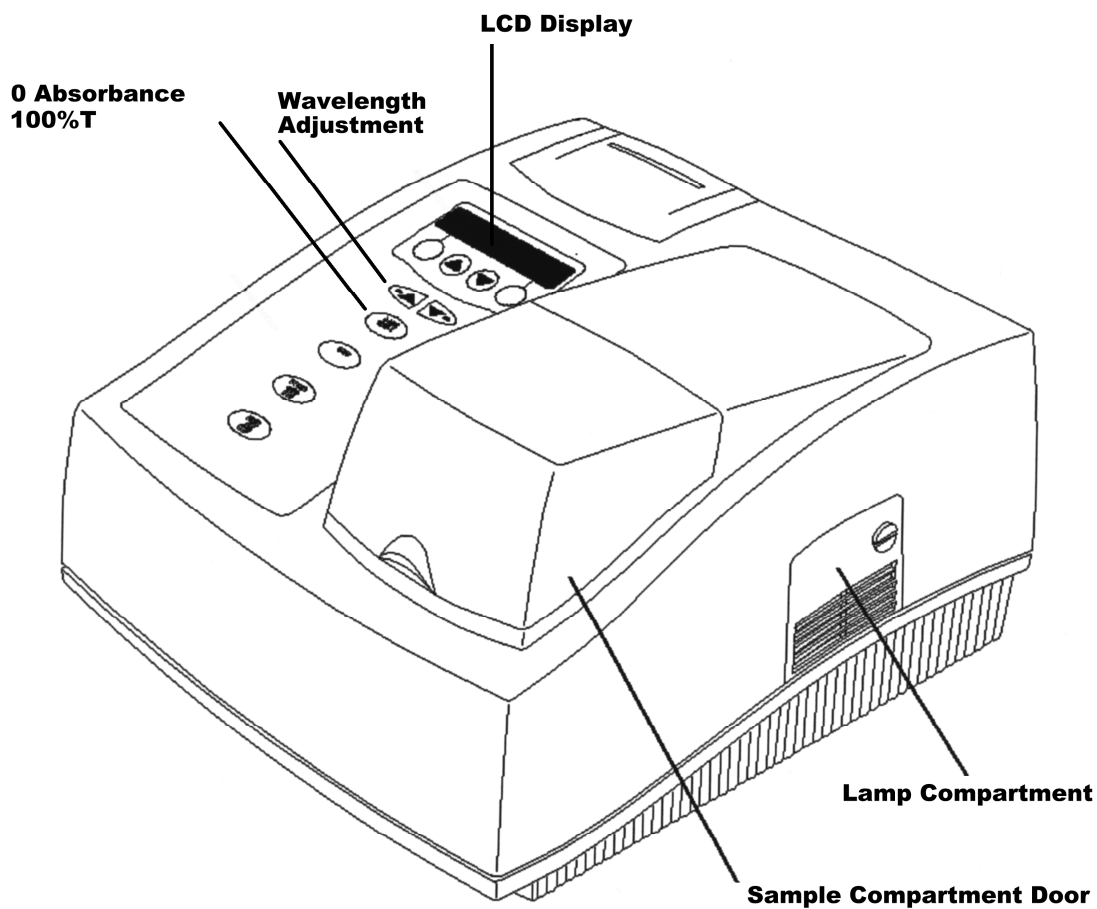
[b] Set the correct wavelength adjustment buttons. Each press of a button changes the wavelength by one nanometer. However, if you hold the button down, it will change more rapidly, and will save wear and tear on the instrument.

[c] Press the 0% absorbance/100% T button. This zeroes the instrument; water has no absorbance and transmits all of the light. This step must be performed each time the wavelength is changed.

[d] Load the second sample tube and record the absorbance.

[e] Change to the next wavelength and repeat steps a-e.

You must record the absorbance of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ from 400-650 nm and the second $[\text{CoCl}_4]^{2-}$ from 550 to 800 nm. You can do these individually or together, as there is some overlap in their spectra.



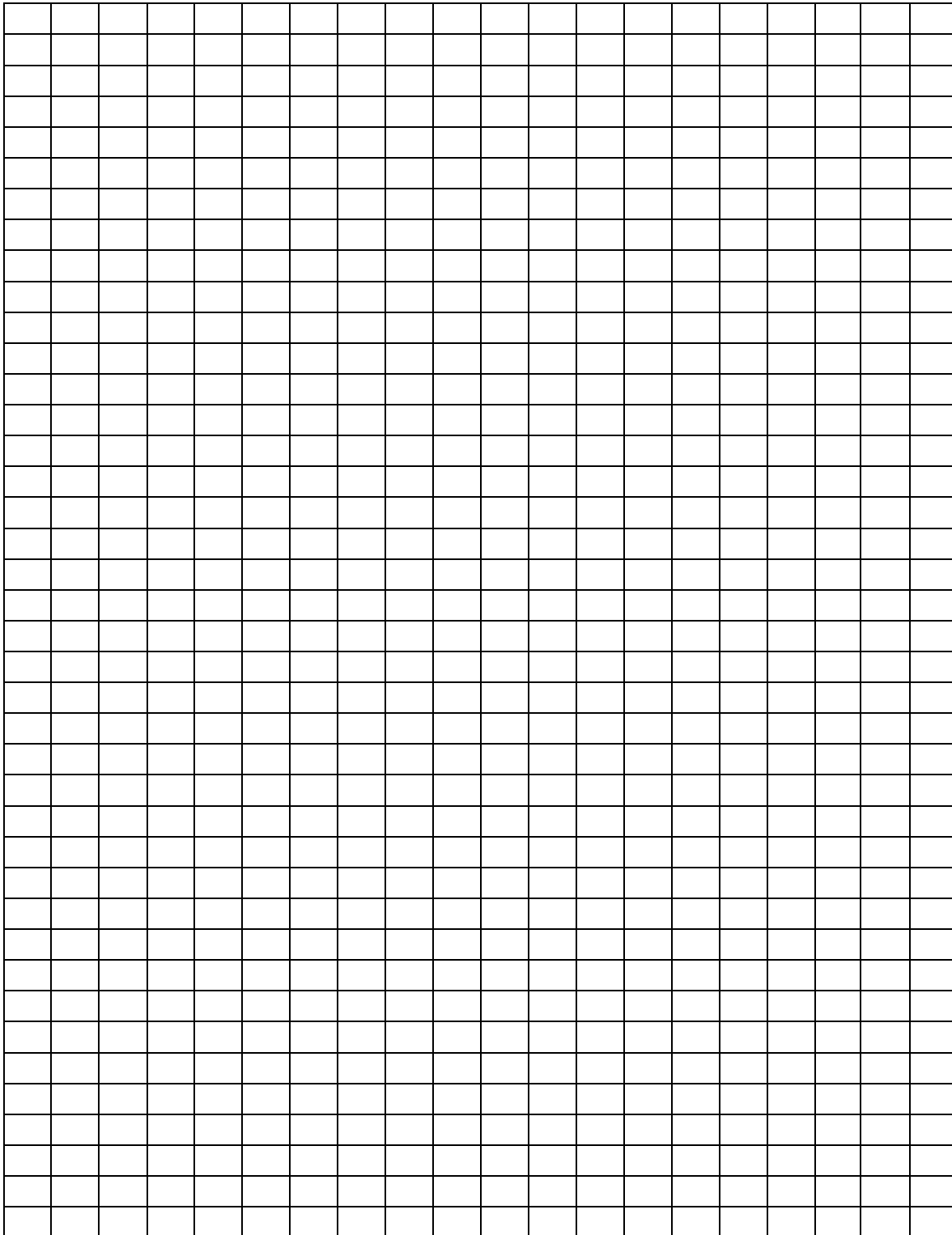
5. Once you have the data, make a plot of absorbance versus concentration for each sample, using the graph paper provided.
6. Identify the wavelength at which each complex absorbs most strongly. Then, using the Beer-Lambert Law, calculate the molar absorptivity of each complex at that wavelength.

Electronic Spectra of Cobalt Complexes Report Page 1	Name:
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Absorbance of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

Wavelength	Absorbance	Wavelength	Absorbance
400		530	
410		540	
420		550	
430		560	
440		570	
450		580	
460		590	
470		600	
480		610	
490		620	
500		630	
510		640	
520		650	

Absorption Spectrum of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

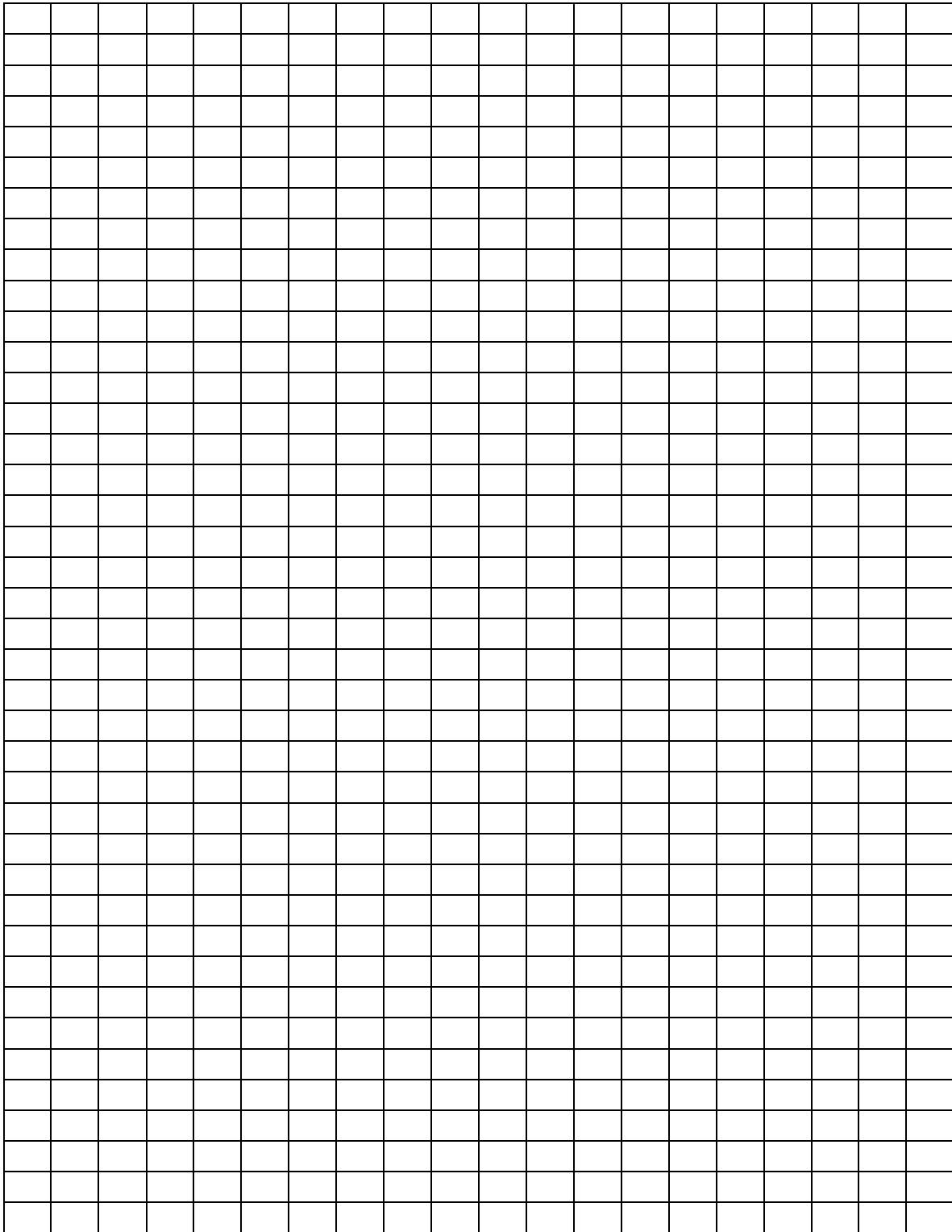


Electronic Spectra of Cobalt Complexes Report Page 3	Name:
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Absorbance of $[\text{CoCl}_4]^{2-}$

Wavelength	Absorbance	Wavelength	Absorbance
550		680	
560		690	
570		700	
580		710	
590		720	
600		730	
610		740	
620		750	
630		760	
640		770	
650		780	
660		790	
670		800	

Absorption Spectrum of $[\text{CoCl}_4]^{2-}$



1. Why do tetrahedral cobalt(II) complexes absorb more strongly than octahedral complexes?
2. Why can you not use ordinary test tubes with the spectrometer?
3. Show your calculations for the concentration of the $[\text{CoCl}_4]^{2-}$ solution used in this experiment.
4. At what wavelength did the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ solution absorb most strongly? What was the molar absorptivity of the complex at this wavelength? Show your calculations below.
5. At what wavelength did the $[\text{CoCl}_4]^{2-}$ solution absorb most strongly? What is the molar absorptivity of this complex? Show your calculations below.