



## CAN I BORROW YOUR BROKEN GOLD NECKLACE FOR MY CHEMISTRY LAB?

### Abstract

A laboratory experiment on the recovery of gold from an obsolete piece of jewelry was developed. The gold leaching system consists of  $K_3[Fe(CN)_6]$  (potassium ferricyanide), NaCl (sodium chloride),  $O_2$  (oxygen) and NaOH (sodium hydroxide);  $K_3[Fe(CN)_6]$  acts as a non-toxic source of cyanide, as well as an oxidizing agent (along with oxygen). Dicyanoaurate ( $[Au(CN)_2]^-$ ) obtained in this process is isolated and characterized by spectroscopic methods. Due to the relative simplicity of this operation and the low toxicity of the reagents required, it can be performed in any educational laboratory. This experiment gives students practice with leaching processes, which are of great importance in the mining industry.

**Keywords:** Hands-On Learning; Inorganic Chemistry; Metallurgy.

## ¿ME PRESTAS TU COLLAR DE ORO ROTO PARA MI PRÁCTICA DE LABORATORIO?

### Resumen

En este artículo, proponemos una práctica de laboratorio utilizando una pieza de joyería de oro dañada. El oro contenido en dicha pieza, es extraído a través de un sistema de lixiviación que consiste de  $K_3[Fe(CN)_6]$  (ferricianuro de potasio), NaCl (cloruro de sodio),  $O_2$  (oxígeno) y NaOH (hidróxido de sodio); el  $K_3[Fe(CN)_6]$  actúa como fuente no tóxica de cianuro, así como agente oxidante junto con el oxígeno. El dicianoaurato ( $[Au(CN)_2]^-$ ) obtenido en este proceso, es aislado y caracterizado por métodos espectroscópicos. Debido a simplicidad de este procedimiento y a la toxicidad baja de los reactivos utilizados, esta práctica puede ser realizada en cualquier laboratorio de docencia. Este experimento permite un acercamiento de los estudiantes hacia procesos de lixiviación, de gran importancia en la industria minera.

**Palabras clave:** enseñanza Experimental; Química Inorgánica; Metalurgia

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## Instructor notes

The leaching experiment was carried out by groups of 15 students, divided into 5 teams. Three laboratory sessions, total of 5 hours, were devoted to the exercise:

### I. First session (2 h)

#### a) Pretreatment of the piece of jewelry

To the approximately 0.40 g of gold jewelry (14 karat), the students add 30 mL of concentrated nitric acid ( $\text{HNO}_3$ ) and stir this mixture under hood for approximately 1.5 h at 50 °C.<sup>1,2</sup> Once the piece has been reduced to dust and the release of nitrogen dioxide ( $\text{NO}_2$ ) is complete, the students stop the stirring.<sup>3,4</sup> Subsequently, the solution (Solution A) is decanted, and the remaining solid (Solid A) is washed three times with 10 mL of distilled water.<sup>5</sup>

#### b) Preparation of the leaching solution

In a 10 mL volumetric flask, the students add 0.83 g (2.5 mmol) of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and 1.17 g of NaCl (20.0 mmol); the salts are dissolved with a pH = 12 solution of NaOH to reach a final volume of 10 mL.

#### c) Leaching reaction

In a 100-mL flask, the students place Solid A and 10 mL of the leaching solution; the mixture is stirred at room temperature for 24 h (Figure 1a-c).<sup>6</sup>

### Important notes:

<sup>1</sup> If the metallic piece contains a stone as part of the structure of the jewelry, and it is difficult to remove it, it does not interfere in the process; at the end of the acid digestion, it is easily removed with a spatula.

<sup>2</sup> Instructors should be especially careful in this step; they should supervise that students wear glasses and gloves to avoid burns with nitric acid.

<sup>3</sup> The time of digestion varies between one sample and another; however, the pieces used by our students were digested in maximum an hour and a half. If during digestion, the sample reaches dryness, more nitric acid must be added. At the end of the digestion, the sample must have the consistency of "syrup".

<sup>4</sup> While the piece of jewelry is being digested, one of the teams prepared 50 mL of the leaching solution using a volumetric flask; 10 mL of this solution are provided to each team. However, each team is requested to perform the calculations to prepare the leaching solution.

<sup>5</sup> The gold obtained must be rinsed with enough water to eliminate nitric acid residues; these can affect the next leaching step. Residues from nitric acid digestion should not be mixed with residues of  $[\text{Fe}(\text{CN})_6]^{3-}$  to prevent the formation of HCN.

<sup>6</sup> After adding the leaching solution to the gold, the laboratory responsible keeps the reaction in agitation for 24 h; the solution obtained is supplied to the students in the next session.



## II. Second session (2 h)

### d) Isolation of $M[Au(CN)_2]$ ( $M = Na, K$ )

Students add 40 mL of water to the leaching reaction; then, the students add 0.57 g (3.75 mmol) of  $FeSO_4$ . Immediately, the resulting solution develops an intense blue color (Figure 1d). Next, students add 5 mL of a NaOH solution of pH = 12;<sup>7</sup> the precipitate is centrifuged at 2000 rpm for 5 min (Note:  $[Au(CN)_2]^-$  is in the solution).<sup>8</sup> Subsequently, students decant the solution and evaporate the water by heating.<sup>9</sup>

### e) Isolation of $[Ag_2O]$

Optionally, silver can be recovered. For this purpose, 10 mL of a saturated solution of NaCl should be gradually added to Solution A. Immediately, a white solid ( $AgCl$ ) precipitates; this solid is separated by filtration and washed 3 times with 5 mL of distilled water. Then, 10 mL of a 5 M solution of NaOH is added to the obtained solid, and the mixture is heated for 15 min at 50 °C. Finally, the brown solid ( $Ag_2O$ ) obtained is washed with distilled water.

### Important notes:

<sup>7</sup> The  $FeSO_4$  should be added first and then the NaOH solution. If the order of adding the reagents is opposite,  $[Fe(CN)_6]^{3-}$  will remain in solution. If by mistake, a team first adds the NaOH solution, it is necessary to neutralize the reaction mixture and repeat the procedure.

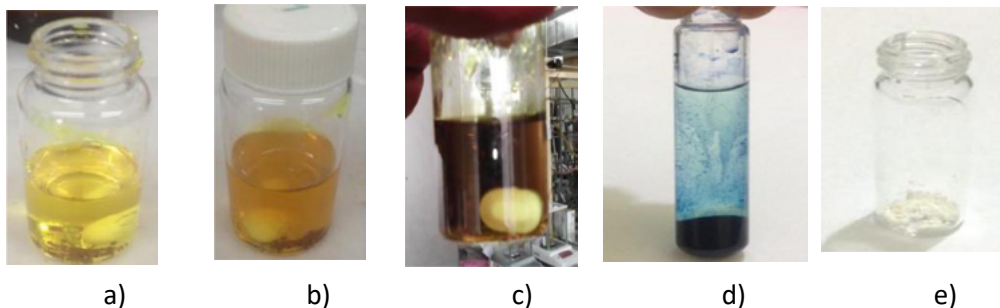
<sup>8</sup> If, after adding the NaOH solution, the solution still has a yellow coloration, it means that iron residues are still exist in the solution; therefore, it is necessary to add NaOH solution until the solution is colorless.

<sup>9</sup> Preferably, the solid should be kept under vacuum for 12 h; this prevents that during the  $[Au(CN)_2]^-$  extraction with methanol (next session), residues of inorganic salts are also extracted. However, those salts do not interfere with the characterization of  $[Au(CN)_2]^-$  by IR and UV spectroscopy.

## III. Third session (2 h)

### f) Extraction and characterization of $[Au(CN)_2]^-$

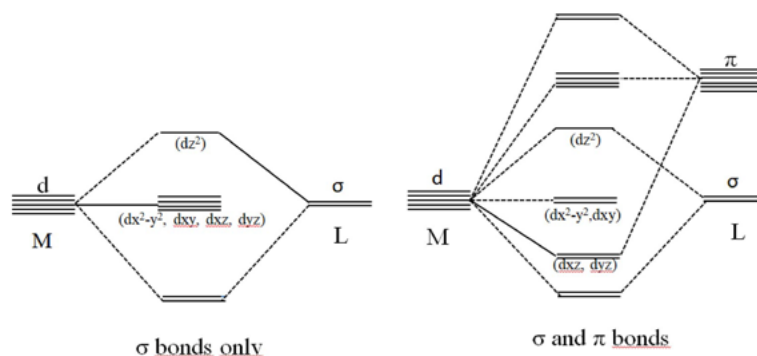
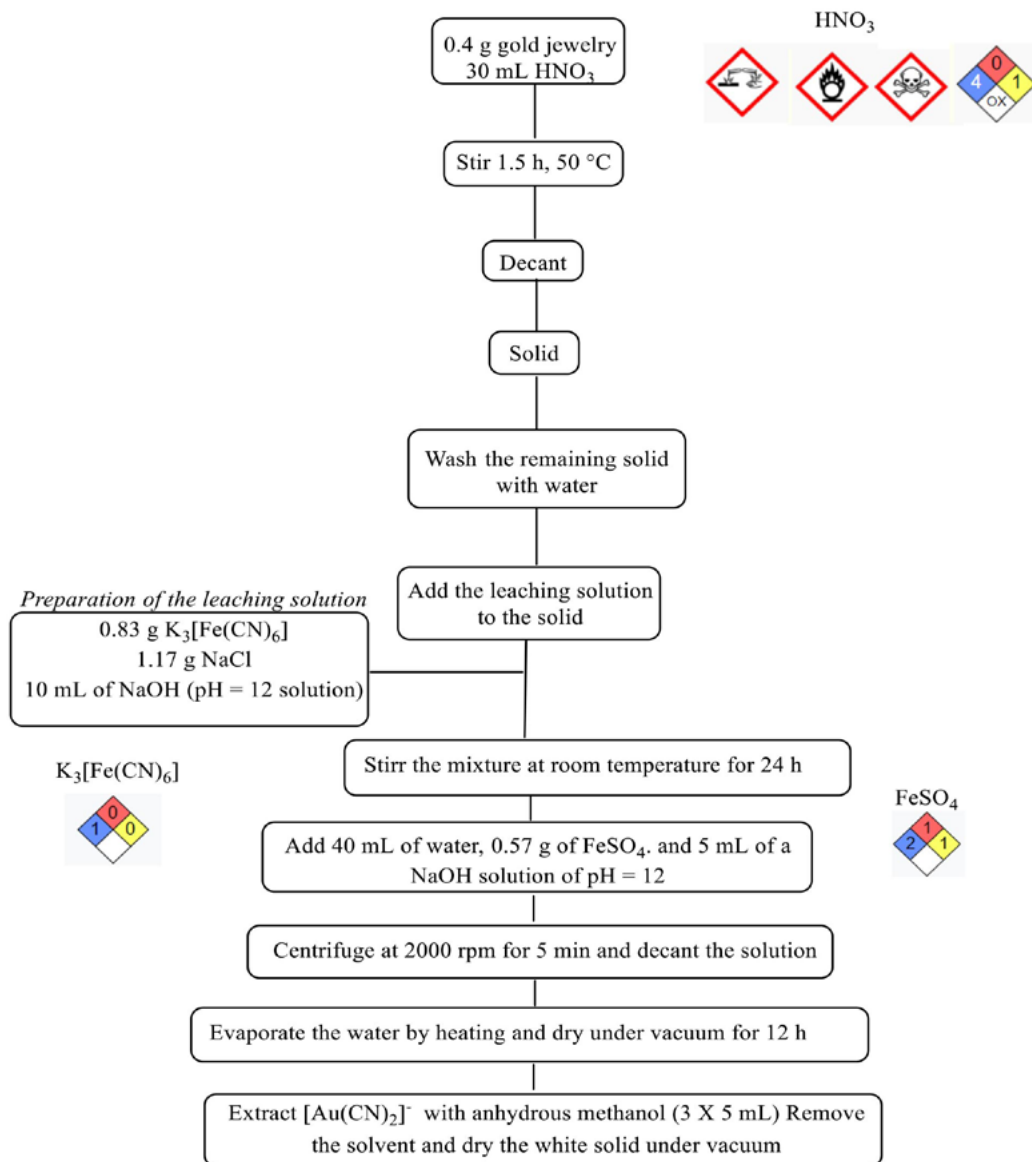
Students extract  $M[Au(CN)_2]$  ( $M = Na, K$ ) with anhydrous methanol (3 X 5 mL). Finally, the solvent is removed, leaving  $M[Au(CN)_2]$  ( $M = Na, K$ ) as a white solid (Figure 1e). The students characterize it by IR and UV spectroscopy. To obtain a UV spectrum with good resolution, it is necessary to prepare a solution between 0.4 mM to 0.7 mM of the final white solid; a sweep of 200 to 300 nm is made (Figure 2). The white solid is also analyzed in an IR spectrophotometer over a range of 400 to 4000  $cm^{-1}$  (Figure 3).



**Figure 1.** Reaction of leaching at a)  $t = 0$ , b)  $t = 10$  min, c)  $t = 24$  h, d) Precipitation of  $KFe[Fe(CN)_6]$  (Turnbull complex), e)  $M[Au(CN)_2]$  ( $M = Na, K$ ).

A summary of the procedure is presented in the following diagram:

### Diagram of the experiment

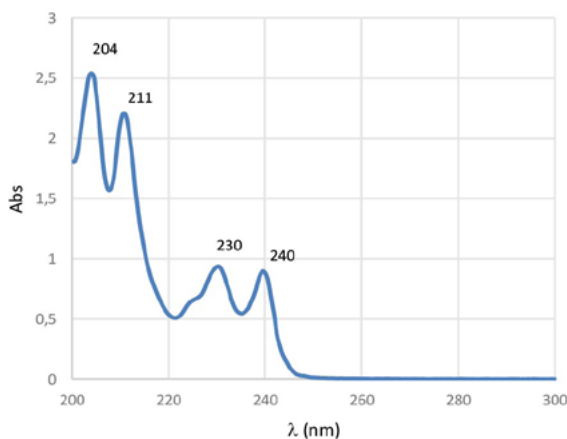


**Figure 2.** Molecular Orbital diagram for a linear complex (simplified)

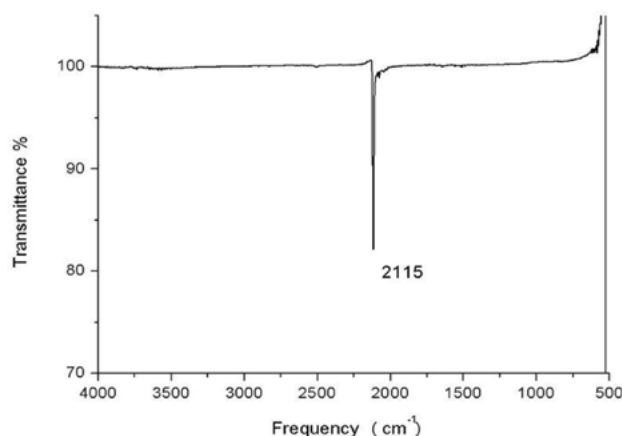


According to the Molecular Orbital Theory, in a linear geometry complex, the  $dz^2$  orbital interacts with the two ligands along the z-axis ( $\sigma$  interactions); the resulting antibonding molecular orbital, with high contribution from the  $dz^2$  orbital, is higher in energy than the original  $dz^2$  orbital; the four remaining  $d$  orbitals do not interact (Figure 2). Additionally,  $CN^-$  is a  $\pi$  acceptor ligand, with empty  $\pi^*$  orbitals that can interact with gold  $dxz$  and  $dyz$  orbitals in a  $\pi$  fashion. The resulting bonding molecular orbitals with high contribution from the  $dxz$  and  $dyz$  orbitals are lower in energy than the original  $dxz$  and  $dyz$  orbitals. Therefore, the coordination of the two cyanide, generates the doubling of the five  $d$  orbitals in three sub-levels,  $2\pi_g(dxz, dyz)$ ,  $\Delta_g(dxy, dx^2-y^2)$  and  $2\sigma_g(dz^2)$ , from lowest to highest energy, respectively (Mason, 1973). In the ion  $[Au(CN)_2]^-$ , the five  $d$  orbitals are full of electrons ( $d^{10}$  complex); thus,  $d$  to  $d$  electronic transitions are not possible. However, transitions between electrons in  $d$  orbitals of the metal and antibonding orbitals of cyanide ( $\pi^*$ ) are possible. These electronic transitions are known as metal to ligand charge transfers (MLCT) (Mason, 1976). For  $[Au(CN)_2]^-$ , four of these transitions have been assigned to electronic transitions  $[2s_g + \pi^* 2p_u]$ ,  $[2s_g + \pi^* 3p_g]$ ,  $[D_g + \pi^* 2p_u]$ , and  $[D_g + \pi^* 3p_g]$ ; the students corroborate the identity of  $[Au(CN)_2]^-$  by observing four bands at 240, 230, 211 and 204 nm, respectively (Figure 2).

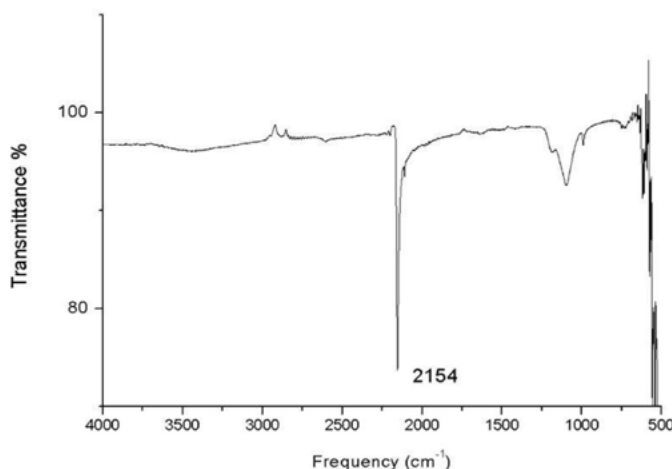
### Representative Spectra



**Figure 3.** UV absorption spectra for  $M[Au(CN)_2]$  ( $M = Na, K$ ).



**Figure 4.** IR Transmission spectra of  $M[Au(CN)_2]$  ( $M = Na, K$ ).



**Figure 5.** IR Transmission spectra of  $K_3[Fe(CN)_6]$ .

## Student handout

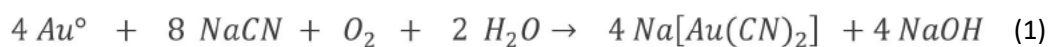
### *Recovery of gold contained in a piece of jewelry*

#### Objectives

- Carry out the leaching of the gold contained in a piece of damaged jewelry, using the leaching system  $K_3[Fe(CN)_6]/NaCl/NaOH$ .
- Characterize by UV and IR spectroscopy, the dicyanoaurate  $M[Au(CN)_2]$  ( $M = Na, K$ ) obtained.
- Analyze the splitting of the “d” orbitals in a complex of linear symmetry.

#### Theory

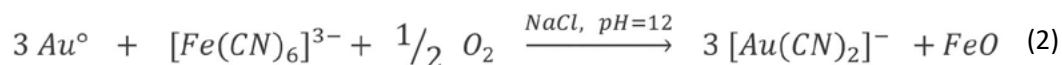
Gold is considered a precious metal because of its high stability against corrosive agents, conductive properties, and unique appearance. It has been used as currency throughout history, in jewelry, and as coating to prevent corrosion of metal surfaces, etc. Gold is found in nature almost exclusively as native gold ( $Au^0$ ) contained in sulfur minerals. The most common methods for extracting gold have involved the use of toxic reagents, for example, forming Hg-Au amalgams where gold oxidation is not required to extract it. Currently, one of the most widely used processes for industrial extraction is “leaching”. This process consists of the oxidation and solubilization of  $Au^0_{(s)}$  in water. The two key factors in a leaching process are the oxidizing agent and the complexing agent, whose function is to stabilize the metal in the aqueous medium. For more than a hundred years, sodium cyanide (NaCN) has been considered the best leaching agent of gold and silver at an industrial level. In this system, the oxidizing agent is oxygen in the environment; the diluted solutions of cyanide dissolve gold according to the following equation:



This process is risky for operators due to the formation of hydrocyanic acid (HCN), which is a highly toxic gas that forms at pH <10 and is volatile at 25 °C. The method presented

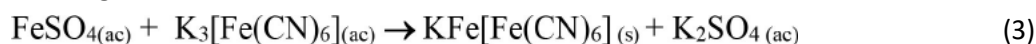


in this lab for gold leaching, uses potassium ferricyanide  $[\text{Fe}(\text{CN})_6]^{3-}$ , which functions as an oxidizing agent and donor of cyanide ions to form the dicyanoaurate  $[\text{Au}(\text{CN})_2]^-$  complex according to the following reaction:



The safety benefit of this method is that the only source of cyanide is  $[\text{Fe}(\text{CN})_6]^{3-}$ , which together with other heavy metals such as Ag, Au, Hg and Pt, are able to form a covalent bond sufficiently strong enough to prevent the formation of HCN. The conditions of this system allow the carbon-iron bonds to be selectively broken, thanks to the presence of a strong electrolyte such as NaCl and the use of a basic pH, which facilitates the transport of electrons and the formation of the  $[\text{Au}(\text{CN})_2]^-$ .

At the end of leaching, the amount of gold in the solution is significantly lower than the amount of  $[\text{Fe}(\text{CN})_6]^{3-}$  that remains unreacted, which interferes with the characterization of the  $[\text{Au}(\text{CN})_2]^-$  complex. This excess is eliminated by adding ferrous sulfate ( $\text{FeSO}_4$ ), producing the precipitation of Turnbull blue (ferric ferrocyanide) according to the following reaction:



Due to the electronic configuration of the complex, it is possible to identify it by means of UV and IR spectroscopies.

Materials	Reagents
Volumetric flask (10 mL)	Gold jewelry piece (approximately 0.4 g)
Beaker (100 mL)	$\text{HNO}_3$
Centrifuge/Tubes for centrifuge	$\text{K}_3[\text{Fe}(\text{CN})_6]$
UV and IR spectrophotometer	NaCl
Stirring plate	NaOH
Magnetic stirrer	$\text{FeSO}_4$
Rotary evaporator (optional)	Anhydrous methanol

## Process

### a) Pretreatment of the piece of jewelry

To approximately 0.40 g of gold jewelry, add 30 mL of concentrated nitric acid ( $\text{HNO}_3$ ); keep this stirring under the hood for approximately 1.5 h. Once the piece has been reduced to dust and the release of nitrogen dioxide ( $\text{NO}_2$ ) is complete, stop the stirring. Subsequently, decant the solution (Solution A), and wash the remaining solid (Solid A) three times with 10 mL of distilled water.

### b) Preparation of the leaching solution

A 10-mL volumetric flask is charged with 0.83 g (2.5 mmol) of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and 1.17 g (20.0 mmol) of NaCl. Finally, add a pH = 12 solution of NaOH to reach a final volume of 10 mL.



### c) Lixiviation and Purification

The leaching solution is added to a beaker (100 mL) with the gold solid; keep this stirring for 24 h at room temperature. Afterwards, 40 mL of water and 0.57 g (3.75 mmol) of  $\text{FeSO}_4$ . Keep the reaction under stirring for 5 min, and then add 5 mL of a NaOH solution at pH = 12. The solution is to be divided in equal parts in centrifuge tubes, and the precipitate is compacted by centrifuging at 2000 rpm for 5 min. Decant the remaining solution, which should be colorless, in a beaker, and remove the solvent by heating (optionally a rotary-evaporator can be used). If possible, keep under vacuum for 12 h to ensure the complete removal of water. Extract the  $[\text{Au}(\text{CN})_2]^-$  with anhydrous methanol (3 X 5 mL); combine the fractions and evaporate the solvent to dryness to obtain a white solid.

### d) Characterization

UV spectroscopy: prepare a solution between  $4 \times 10^{-4}$  to  $7 \times 10^{-4}$  mol/L and scan from 200 to 300 nm. Compare the spectrum obtained with the spectrum reported in the reference.

IR spectroscopy: the white solid is analyzed in a range of 400 to 4000  $\text{cm}^{-1}$ .

## Pre-lab Questionnaire

1. What is a leaching process?
2. What advantages does the leaching system used in this experiment offer with respect to the traditional process using NaCN?
3. What are the toxicity indices of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and NaCN?
4. Calculate the number of valence electrons, the number of non-binding electrons, and the oxidation state of  $[\text{Au}(\text{CN})_2]^-$  complex.

## Post-lab Questionnaire

1. Which metals could form a compound analogous to the  $[\text{Au}(\text{CN})_2]^-$  complex?
2. How many bands are observed in the UV spectrum and to which transitions are each due?
3. The ligands are classified as  $\pi$ -acceptors or  $\pi$ -donors. What type of ligand is the cyanide ion?