2024-2025学年春夏学期《无机及分析化学实验》实验报告

实验名称：Synthesis and Characterization of Three Kinds of Cobalt-ammine Coordination Compounds. 姓名/同组同学：_____ 实验时间：

2025 年 4 月 29 日 & 5 月 6 日 指导老师/助教：_____/_____ 第 1 页

Ⅰ. Objectives

(1). Know the fundation of coordination chemistry.

(2). Synthesize three different cobalt-amine coordination compounds.

(3). Determine the cobalt content in the products using iodometry.

(4). Analyze the ion configurations of the products using conductometry

(5). Measure the crystal field splitting energy of the products using spectrophotometry.

Ⅱ. Principles

There are many isomers (异构体) of cobalt coordination compounds due to their inner composition: $[Co(NH_3)_5Cl]Cl_2$ $[Co(NH_3)_6]Cl_3$、$[Co(NH_3)_5H_2O]Cl_3$. Under the catalysis of activated charcoal and the oxidation of H_2O_2, $[Co(NH_3)_6]Cl_3$ can be synthesized using cobalt (II) chloride ($CoCl_2$) and concentrated ammonium solution ($NH_3 \cdot H_2O$) as starting materials. $[Co(NH_3)_6]Cl_3$ crystals can be precipitated from a concentrated hydrochloric acid (HCl) solution.

- By adjusting the reaction temperatures, $[Co(NH_3)_5H_2O]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ can be synthesized from the same raw material without the need for activated charcoal.

$$2CoCl_2 + 10NH_3 + 2NH_4Cl + H_2O_2 \xrightarrow[\text{charcoal}]{\text{activated}} 2[Co(NH_3)_6]Cl_3 + 2H_2O$$

$$2CoCl_2 + 8NH_3 + 2NH_4Cl + H_2O_2 = 2[Co(NH_3)_5Cl]Cl_2 + 2H_2O$$

$$2CoCl_2 + 8NH_3 + 2NH_4Cl + H_2O_2 = 2[Co(NH_3)_5H_2O]Cl_3$$

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$$

· Iodometry is used to determine the cobalt content in the products. When boiled in an excess strong alkaline solution (强碱溶液), cobalt (Ⅲ) coordination compound decomposes (分解) to forms $Co(OH)_3$.

$$2[Co(NH_3)_6]Cl_3 + 6NaOH = 2Co(OH)_3 + 12NH_3\uparrow + 6NaCl$$

$$2[Co(NH_3)_5Cl]Cl_2 + 6NaOH = 2Co(OH)_3 + 10NH_3\uparrow + 6NaCl$$

$$2[Co(NH_3)_5H_2O]Cl_3 + 6NaOH = 2Co(OH)_3\downarrow + 10NH_3\uparrow + 6NaCl + 2H_2O$$

· Oxidizing properties, $Co(OH)_3$ can oxidize I^- to I_2

The iodine produced can be titrated using a standard $Na_2S_2O_3$ solution. Co content in the products is determined.

$$2Co(OH)_3 + 2I^- + 6H^+ = 2Co^{2+} + I_2 + 6H_2O$$

$$2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-$$

The conductivity of each cobalt (Ⅲ) coordination compound can be measured using a conductivity meter, allowing its ion configuration to be deduced.

molar conductivity & ion configuration

ion configuration	ion number	Conductivity Λ ($\mu S \cdot cm^{-1}$)
MA	2	120~134
MA_2 or M_2A	3	240~278
MA_3 or M_3A	4	411~451
MA_4 or M_4A	5	533~569.

Ⅲ.Pre-lab Questions

(1). What are the functions of H_2O_2, $NH_3 \cdot H_2O$ and concentrated HCl in the synthesis procedures?

① H_2O_2: Work as an oxidizing agent, usually the cobalt is Co^{2+}. And the raw material we use is $CoCl_2$, so adding H_2O_2 can turn it into Co^{3+}

$$2Co^{2+} + H_2O_2 + 2NH_4^+ \longrightarrow 2Co^{3+} + 2NH_3 + 2H_2O$$

②. $NH_3 \cdot H_2O$: Provide NH_3 to coordinate with Co^{3+} also provide OH^- environment to react with the excess H^+.

③. concentrated HCl: Provide Cl^- to form coordination compounds. And High Cl^- concentration can stabilize the compounds.

(2). What is the difference between iodometry and iodimetry? What are the key points to prevent the measurement error of iodometry in this experiment?

① Iodimetry (直接碘量法): Use standard I_2 solution to titrate reducing substances, and the I_2 is reduced to I^-

②. Iodometry (间接碘量法): First use oxidizing substances to react with excess KI, which will produce I_2. Then use $Na_2S_2O_3$ standard solution to react with the I_2.

To prevent the measurement error of iodometry in this experiment, we should ensure the excess KI to make it react fully. Also, keep the solution's pH to reduce vice reaction.

(3). Give the determination principle of cobalt content in the product.

Under OH^- environment, the 3 kinds of Cobalt-ammine coordination compounds can be turned into $Co(OH)_3$.
The $Co(OH)_3$ react with I^- to generate Co^{2+} & I_2.
Measure the I_2 which we can know the exact Co content in the products.
Also, we can know the ion configuration by the conductivity.

Ⅳ.Procedures

1. Synthesis of $[Co(NH_3)_6]Cl_3$.

100mL Erlenmeyer flask → NH_4Cl 4.0g → $CoCl_2 \cdot 6H_2O$ 6.0g → H_2O 8mL → swirl to mix well →
heat in a water bath at 60°C for 10 min → cool to RT → activated charcoal 0.4g
Swirl for several minutes → conc. $NH_3 \cdot H_2O$ 10mL (add slowly while swirling gently) → keep in ice bath → H_2O_2 8mL →
heat in a water bath at 60°C for 15 min → suction filtration → get the sediment.(沉淀物)
100mL beaker → sediment → boiling HCl (3+50) 40~60 mL → stir quickly → suction filtration → filtrate solution → 100mL beaker → conc. HCl 10mL → mix well → cool in an ice bath → suction filtration → place the product in a watch glass → dry at 90°C for 20~30min → weigh and record the mass

ps. (1). Weigh the activated charcoal carefully.

(2). Maintain the Erlenmeyer flask at around 60°C, swirling it ~~occ~~ occasionally to help the reaction reach completion.

(3). Prepare the boiling HCl (3+50) just before use by adding 3 droppers of concentrated HCl to 50mL boiling water.

2. Synthesis of $[Co(NH_3)_5Cl]Cl_2$.

100mL Erlenmeyer flask $\xrightarrow[2.0g]{NH_4Cl}$ $\xrightarrow[13mL]{conc.\ NH_3\cdot H_2O}$ swirl to mix well $\xrightarrow[4.0g]{CoCl_2\cdot 6H_2O}$ earthy red ↓ ⟶ cool to RT $\xrightarrow[12mL]{H_2O_2}$ add slowly while swirling gently ⟶ deep red mixture $\xrightarrow[15mL]{conc.\ HCl}$ purple red crystals ⟶ heat in a water bath at 80°C for 20min ⟶ cool in an ice bath ⟶ suction filtration ⟶ place the product in a watch glass ⟶ dry at 90°C for 20~30min ⟶ weigh and record the mass.

ps. Keep the Erlenmeyer flask at around 80°C, swirling it occasionally to help the reaction reach completion.

3. Standardization of 0.1 mol/L $Na_2S_2O_3$ Solution.

Using KIO_3 as a primary standard.

150mL Erlenmeyer flask $\xrightarrow[20.00mL]{KIO_3}$ $\xrightarrow[0.7g]{KI}$ swirl until solids dissolve completely $\xrightarrow[5mL]{3\ mol/L\ H_2SO_4}$ $\xrightarrow[70mL]{H_2O}$ purplish red $\xrightarrow{Na_2S_2O_3}$ titrate to pale yellow $\xrightarrow[2mL]{starch}$ deep blue $\xrightarrow{Na_2S_2O_3}$ titrate until colorless ⟶ read final volume ⟶ repeat 2 more times.

4. Determination of the Cobalt Content in the Product.

250mL iodine flask → product 0.4g → 5mol/L NaOH 20mL → boiling chip 3~4 grains → heat to boiling for 25 min → add water occasionally → cool to RT → KI 0.8g → gently swirl for 1min → 6mol/L HCl 20mL → keep in the dark for 25 min → H_2O 70mL → titrate fast with $Na_2S_2O_3$ until light orange → starch 2mL → deep blue → titrate slowly with $Na_2S_2O_3$ until solution turns pink → record the volume → repeat two more times

5. Determination of the Ion Configuration of Coordination Compounds.

(1). Use a 100mL volumetric flask to prepare 100mL of 1.0×10^{-3} mol/L product solution.

(2). Measure the conductivity of the solution using a conductivity meter.

(3). Determine the ion configurations of the coordination compounds using the known data.

Ⅴ.Data Record Tables

Table synthesis of cobalt(III) coordination compound

molecular formula of product	NH_4Cl /g	$CoCl_2\cdot6H_2O$ /g	$NH_3\cdot H_2O$(concn.) /mL	HCl(concn.) /mL	actual output /g
$[Co(NH_3)_6]Cl_3$	3.99	6.02	10.0	10.0	0.43
theoretical output /g	brief description of product				
7.02.					

Table determination of cobalt content in the products

	1	2	3
m(product)/g	0.4021	0.3986	0.4010
$V_1(Na_2S_2O_3)$/mL	0.75	0.71	2.92
$V_2(Na_2S_2O_3)$/mL	13.60	13.30	15.88
$\Delta V(Na_2S_2O_3)$/mL	12.85	12.59	12.96

Table 3 determination of the concentration of 0.1 mol·L^{-1} $Na_2S_2O_3$ standard solution

	1	2	3
$m(KIO_3)$/g		0.3060	
$V_1(Na_2S_2O_3)$/mL	0.40	0.90	1.10
$V_2(Na_2S_2O_3)$/mL	16.40	16.80	16.80
$\Delta V(Na_2S_2O_3)$/mL	16.00	15.90	15.70

Table 4 determination of the structure of cobalt (III) complex ion

product	m/g	Conductivity (×1 ~~mol·m^{-3}·mol^{-1}~~ μS·cm^{-1})
$[Co(NH_3)_6]Cl_3$	0.0268	572
$[Co(NH_3)_5Cl]Cl_2$	0.0274	391
$[Co(NH_3)_5H_2O]Cl_3$	0.0270	398

Table 5 determination of crystal field splitting of cobalt (III) complex

product	λ_{max}/nm	Δ_0/kJ·mol^{-1}
$[Co(NH_3)_6]Cl_3$	474	
$[Co(NH_3)_5Cl]Cl_2$	530	
$[Co(NH_3)_5H_2O]Cl_3$	497	

Table synthesis of cobalt(Ⅲ) coordination compound

Product	NH_4Cl/g	$CoCl_2 \cdot 6H_2O$/g	$NH_3 \cdot H_2O$/mL	HCl /mL	actual output /g
$[Co(NH_3)_5Cl]Cl_2$	2.00	4.01		15.0	4.05
theoretical output /g		brief description of product.			
4.22					

Ⅵ. Key Steps and Precautions

1. Weigh the activated charcoal carefully, as it is easy to spill.
2. To let the reaction among $CoCl_2$, NH_3, NH_4Cl and H_2O_2 completely, maintain the temperature and swirl the Erlenmyer flask occasionally to help the reaction reach completion.
3. Ensure that no yellow solids remain in the reaction solution before performing suction filtration
4. Before the titration step, don't use tap water to wash the burette. Rinse it with deionized water.
5. Keep the Erlenmeyer flask at around 80℃, swirling it occasionally to help the reaction reach completion.
6. When preparing the $[Co(NH_3)_5H_2O]Cl_3$, maintaining a low temperature is crucial. The Erlenmeyer flask must be kept in an ice bath at all times.
7. When using the iodine flask, be cautious when to cover it and uncover it.
8. Before adding the starch solution, titrate quickly and swirl gently. But titrate slowly and swirl vigorously after adding the starch solution to release the absorbed I_2.

Ⅶ.Results and Data Processing

According to the recorded data, we can get the following tables.

Table 1 synthesis of cobalt(III) coordination compound

molecular formula of product	NH_4Cl /g	$CoCl_2 \cdot 6H_2O$ /g	$NH_3 \cdot H_2O$(concn.) /mL	HCl(concn.) /mL	actual output /g
$[Co(NH_3)_6]Cl_3$	3.99	6.02	10.0	10.0	0.43

theoretical output /g	yield/%	brief description of product
7.02	6.1	Orange powder

molecular formula of product	NH_4Cl /g	$CoCl_2·6H_2O$ /g	$NH_3·H_2O$(concn.) /mL	HCl(concn.) /mL	actual output /g
$[Co(NH_3)_5Cl]Cl_2$	2.00	4.01	0	15.0	4.05
theoretical output /g	yield/%	brief description of product			
4.22	96.0	Purple powder			

The yield of the two products is: yield($[Co(NH_3)_6]Cl_3$)=$\frac{\text{actual output}}{\text{theoretical output}} \times 100\% = \frac{0.43}{7.02} \times 100\% = 6.1\%$

yield($[Co(NH_3)_5Cl]Cl_2$)=$\frac{\text{actual output}}{\text{theoretical output}} \times 100\% = \frac{4.05}{4.22} \times 100\% = 96.0\%$

Table 2 determination of cobalt content in the products

	1	2	3
m(product)/g	0.4021	0.3986	0.4010
$V_1(Na_2S_2O_3)$/mL	0.75	0.71	2.92
$V_2(Na_2S_2O_3)$/mL	13.60	13.30	15.88
$\Delta V(Na_2S_2O_3)$/mL	12.85	12.59	12.96
ω(Co含量)/%	18.83	18.61	19.04
$\overline{\omega}$(Co)/%	18.82		
$\overline{d_r}$ /%(average)	0.78		
ω(Co)/%(theory)	23.53		
ρ(产品纯度)/%	79.98		

$\omega(\text{Co含量})_1=\frac{\Delta V(Na_2S_2O_3)\cdot 0.1000\text{mol/L}\cdot Mr(Co)}{m} \times 100\% = \frac{12.85\times10^{-3}\times0.1000\times58.93}{0.4021} \times 100\% = 18.83\%$

$\omega(\text{Co含量})_2=\frac{\Delta V(Na_2S_2O_3)\cdot 0.1000\text{mol/L}\cdot Mr(Co)}{m} \times 100\% = \frac{12.59\times10^{-3}\times0.1000\times58.93}{0.3986} \times 100\% = 18.61\%$

$\omega(\text{Co含量})_3=\frac{\Delta V(Na_2S_2O_3)\cdot 0.1000\text{mol/L}\cdot Mr(Co)}{m} \times 100\% = \frac{12.96\times10^{-3}\times0.1000\times58.93}{0.4010} \times 100\% = 19.04\%$

$\overline{\omega}(\text{Co})=\frac{\omega(\text{Co含量})1+\omega(\text{Co含量})2+\omega(\text{Co含量})3}{3} = \frac{18.83\%+18.61\%+19.04\%}{3} = 18.82\%$

$$\overline{d_r} = \frac{\frac{\sum_{i=1}^{3}|\omega i - \overline{\omega}|}{3}}{\overline{\omega}} \times 100\% = \frac{\frac{|18.83\% - 18.82\%| + |18.61\% - 18.82\%| + |19.04\% - 18.82\%|}{3}}{18.82\%} \times 100\%$$

$$= 0.78\%$$

ω(Co)(theory)=$\frac{\mathrm{M(Co)}}{\mathrm{M([Co(NH_3)_5Cl]Cl_2)}} \times 100\% = \frac{58.93}{250.48} \times 100\% = 23.53\%$

ρ(产品纯度)=$\frac{\overline{\omega}(\mathrm{Co})}{\omega(\mathrm{Co})(\mathrm{theory})} \times 100\% = 79.98\%$

Table 3 determination of the concentration of 0.1 mol·L^{-1} $Na_2S_2O_3$ solution

	1	2	3
m(KIO_3)/g	0.3060		
V_1($Na_2S_2O_3$)/mL	0.40	0.90	1.10
V_2($Na_2S_2O_3$)/mL	16.40	16.80	16.80
ΔV($Na_2S_2O_3$)/mL	16.00	15.90	15.70
c($Na_2S_2O_3$)/mol·L^{-1}	0.1072	0.1079	0.1093
c($Na_2S_2O_3$)/mol·L^{-1}(average)	0.1081		
d_r/%(average)	0.7092		

c(KIO_3)=$\frac{m}{214\times0.100} = 0.0143$ mol/L; c($Na_2S_2O_3$)$_1$=$\frac{0.0143\times20.00\times10^{-3}\times3\times2}{16.00\times10^{-3}} = 0.1072$ mol/L

c($Na_2S_2O_3$)$_2$=$\frac{0.0143\times20.00\times10^{-3}\times3\times2}{15.90\times10^{-3}} = 0.1079$ mol/L ; c($Na_2S_2O_3$)$_3$=$\frac{0.0143\times20.00\times10^{-3}\times3\times2}{15.70\times10^{-3}} = 0.1093$ mol/L

c($Na_2S_2O_3$) (average)=$\frac{0.1072+0.1079+0.1093}{3} = 0.1081$ mol/L

d_r(average)= $\frac{\frac{\sum_{i=1}^{3}|ci-\overline{c}|}{3}}{\overline{c}} \times 100\% = \frac{|0.1072-0.1081|+|0.1079-0.1081|+|0.1093-0.1081|}{3\times0.1081} \times 100\% = 0.7092\%$

Table 4 determination of the structure of cobalt (III) complex ion

product	m/g	Concentration /mol·L^{-1}	conductivity ($\times\mu s \cdot cm^{-1}$)	molar conductivity ($\times10^{-4}$·m^{-2}·mol^{-1})	ion configuration
$[Co(NH_3)_6]Cl_3$	0.0268	1.00×10^{-4}	572	5720	MA_4
$[Co(NH_3)_5Cl]Cl_2$	0.0274	1.09×10^{-4}	391	3587	MA_3
$[Co(NH_3)_5H_2O]Cl_3$	0.0270	1.00×10^{-4}	398	3980	MA_3

c($[Co(NH_3)_6]Cl_3$)=$\frac{0.0268}{267.5} = 1.00\times10^{-4}$ mol/L; c($[Co(NH_3)_5Cl]Cl_2$)=$\frac{0.0274}{250.5} = 1.09\times10^{-4}$ mol/L

c([$Co(NH_3)_5H_2O$]Cl_3)=$\frac{0.0270}{268.5} = 1.00 \times 10^{-4}$ mol/L

Table 5 determination of the crystal field splitting energy of cobalt (III) complex

product	λ_{max}/nm	Δ_0/kJ·mol^{-1}
[$Co(NH_3)_6$]Cl_3	474	4.19×10^{-22}
[$Co(NH_3)_5Cl$]Cl_2	530	3.75×10^{-22}
[$Co(NH_3)_5H_2O$]Cl_3	497	4.00×10^{-22}

Δ_0=$\frac{hc}{\lambda_{max}} = 4.19 \times 10^{-22}$. The following two are the same equation to calculate.

Ⅷ.Analysis, Discussion and Summary

Error analysis:

In the experiments, the yield of [$Co(NH_3)_6$]Cl_3 is so low, but the [$Co(NH_3)_5Cl$]Cl_2 is somehow higher. And the cobalt content in the [$Co(NH_3)_5Cl$]Cl_2 is also lower. Here are the possible reasons of the errors:

1. When preparing the [$Co(NH_3)_6$]Cl_3, the addition of HCl maybe excess. This causes more usage of NH_3, and there's not enough NH_3 to coordinate with Co^{3+}.
2. The ice bath didn't make the products generate sediment well.
3. During using the boiling water to make HCl, there may some HCl evaporate away.
4. When preparing the [$Co(NH_3)_6$]Cl_3, two times' suction filtrations are needed. This cause more wastage.
5. The yield of [$Co(NH_3)_5Cl$]Cl_2 is higher. This may due to the drying time is short that the product is wet.
6. When adding the concentrated HCl solution, a amount of steam is generated. This means that the HCl solution also wastes some HCl.
7. The [$Co(NH_3)_5Cl$]Cl_2 product isn't completely wet which leads weighing error and the cobalt content in the [$Co(NH_3)_5Cl$]Cl_2 is lower.
8. When using iodometry, there always exists I_2 evaporate away from the system.
9. The adding and swirling speed during the iodometry is not easy to control. The swirling and adding speed may a bit quicker which causes higher concentration.

Summary:

1. Be cautious to the usage of added solution or solid, this may cause the whole yield of the product.
2. When titrating, notice the adding speed of the solution.
3. Iodometry and iodimetry are two ways to determine the ions content.
4. Using various ways to determine the contents and strcuture can help us get more convincing results.

Ⅸ. Post-lab Questions

(1) If the conductivity results of the products are higher or less than the theoretical ones, give an explanation.

The conductivity is higher: There may exist other ions and the additional ions may disturb the conductivity. After the use of conductivity meter, it may don't washed well. The residual ions can affect the conductivity.

The conductivity is lower: The coordination compound in the solution may undergo hydrolysis or other side reactions. Moreover, the cobalt-ammine coordination compounds may form aggregates or larger-sized complexes in solution. They can all decrease the ions' number in the solution, and then decrease the conductivity.

(2) Which λ_{max} is highest among the three cobalt (III) coordination compounds synthesized in the experiment? You should take the spectrochemical series of ligands into account.

According to the spectrochemical series of ligands, we can know that $Cl^- < H_2O < NH_3$. The ligands of $[Co(NH_3)_6]Cl_3$ is NH_3. The ligands of $[Co(NH_3)_5Cl]Cl_2$ is NH_3 and Cl^-. The ligands of $[Co(NH_3)_5H_2O]Cl_3$ is NH_3 and H_2O. Therefore, the crystal field splitting energy is $[Co(NH_3)_6]Cl_3 > [Co(NH_3)_5H_2O]Cl_3 > [Co(NH_3)_5Cl]Cl_2$. Also, due to the equation: $\Delta_0=\frac{hc}{\lambda_{max}}$ we know that the higher λ_{max}, the lower crystal field splitting energy. So, $[Co(NH_3)_5Cl]Cl_2$ has the highest λ_{max}.

Ⅹ. Appendix

Here are some pictures which show the experimental phenomena during the process and data records.

Fig. 1 The filter residue in Synthesis of $[Co(NH_3)_6]Cl_3$

From the figures, we can see some orange residue mixed with the activated charcoal. They may the cobalt mixture. And from this figure, we can explain the low yield of $[Co(NH_3)_6]Cl_3$.

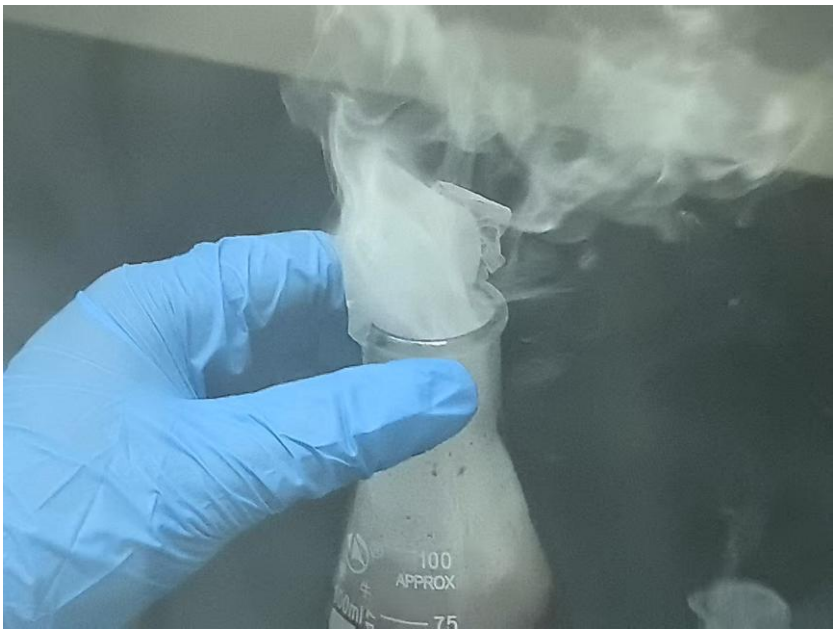

Fig. 2 The white smoke after adding concentrated HCl

This figure shows the generated white smoke immediately after adding the concentrated HCl. This indicates the loss of HCl and explain the low yield in some way.

Fig. 3 The $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ products

Fig. 4 The Light absorption curve of three kinds of cobalt-ammine coordination compounds

From the curves we can know the λ_{max} to calculate the crystal field splitting energy.

评分项目	学术规范	书写工整	写作表达	数据结果和分析讨论	课前和课后思考题	总分
分值	30 分	10 分	10 分	30 分	20 分	100 分
得分/分						
评语						