

Assessment of Greenness of Various Routes of Synthesis of *cis* and *trans* Isomers of Bis(glycinato)copper(II) Monohydrate: An Undergraduate Chemistry Experiment

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Abstract Synthesis of *cis* and *trans* isomers of bis(glycinato)copper (II) monohydrate is a standard experiment performed in undergraduate curriculum. Awareness on green chemistry on the other hand is also another important topic for undergraduate students. The aim of this paper is to introduce these two important aspects through a unified protocol, which was executed by an undergraduate student as summer project. The focus of this study is to present the results of the evaluation of greenness of the synthetic routes traditionally used for the synthesis of *cis/trans* copper glycinato complexes at undergraduate labs. The evaluation tables should help the educators to present an overview of greenness of different preparative methodologies before the students. Each of the two geometrical isomers had been prepared via two different routes available in literatures. The greenness had been assessed in accordance with the 12 principles of Green Chemistry formulated by Paul Anastas and John Warner. A tabular form of the Green Chemistry Mass Metrics is presented along with and other holistic graphic metrics such as the Green Star and the Green Circle, the latter being based on the Globally Harmonized System (GHS) of Classification and Labelling of Chemicals. Further, SWOT tables (Strengths, Weakness, Opportunities and Threats) have been included to expose the upshots and drawbacks of the different synthetic routes.

Keywords: green chemistry, coordination compounds, synthesis, stereochemistry

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1. Introduction

Green Chemistry is a very important field of study. The major goal of green chemistry, is the sustainable development and production of chemicals by minimizing the use of hazardous substances, which poses higher risk towards environment. [1] With increasing focus on the environmental impact of chemical substances, it is important to study the greenness of the synthetic routes of various compounds that are important in our daily life. [2,3,4,5] Even though the 12 principles of Green Chemistry, formulated by Anastas and Warner, are well known today [6], the scrutiny of a synthetic route for greenness is still very complex and impractical. To overcome this hurdle, the applications of a universal set of green matrices to evaluate material efficiencies of chemical transforms, is already well known. [7,8,9,10] Such metrics had already been in use by many research groups for accessing the relative performances of multiple routes for a specific target molecule. [11,12,13] In our present study, aid of simple Green Chemistry Mass Metrics had been taken, for the evaluation of greenness of

different synthetic routes and to determine the greenest route. [14,15,16] Construction of the Green Star and the Green Circle were achieved through the Globally Harmonized System of Classification and Labelling of Chemicals. Green star and Green Circle, both can provide visual insight into the greenness of the various synthetic routes. [17,18] This is an instrumental tool in the undergraduate courses [19] not only as an exercise in the laboratory, but also to install the feeling of concern about the hazards of traditional processes and to align the students towards the advantages of green and safe chemistry. [20,21]

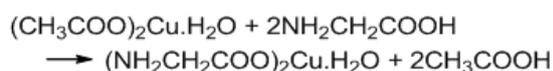
Copper serves as an essential element in our life cycle [22] and metabolism of copper in living organisms is definitely needed to be understood. In an effort to understand the mechanism of metabolism of copper in living systems, many copper amino-acid complexes have been extensively studied as prototypes. [23,24] Moreover the study of Cu-glycinato complexes serves as an example of geometrical isomerism in coordination compounds. These complexes also can be used for introduction of the concept group theory and symmetry elements present in molecules to the undergraduate students. Therefore, preparation of *cis/trans* (glycinato)copper(II)monohydrate complexes had

traditionally been included in undergraduate curriculum for decades. In this era, where green chemistry teaching, is very important, while choosing the methods for preparation of *cis/trans* Cu-glycinate complexes, it is worthwhile to look into perspective of greenness of different preparative routs. The data for evaluation of greenness of different protocols were accomplished using the data obtained by preparation of the complexes using the common methods available in literatures.

2. Discussions on Synthetic Methodology

In our present study, we had dealt with the preparation of copper salts of the simplest amino acid, glycine, which is well known experiment in undergraduate study. Copper bisglycinate monohydrate is a blue compound which can exist as two geometrical isomers, the *cis* and the *trans* copper glycinate monohydrate.

Glycine, when deprotonated (as glycinate ion, $\text{NH}_2\text{CH}_2\text{COO}^-$, abbreviated as gly), is capable of forming two coordination bonds to the central metal ion (in this case copper(II)), through the nitrogen and oxygen atoms. Hence, it functions as a chelating bidentate ligand and favors the formation of bis(glycinate)copper(II) complex. In the reaction between copper(II) acetate monohydrate and glycine, the dissociation of glycine molecule produces glycinate anion, $\text{NH}_2\text{CH}_2\text{COO}^-$ (gly), which is a bidentate ligand and easily replaces the monodentate acetate ion, CH_3COO^- in the copper complex. The dissociated proton from glycinate ion is accepted by the acetate ion and hence acetic acid is produced in the reaction between copper(II) acetate monohydrate and glycine.



Scheme 1.

However, both the isomers exist as an equilibrium mixture. But in an ethanolic solution at around 70°C, the *cis* isomer precipitates much quicker compared to the *trans* isomer, and hence leading to a shift in equilibrium away from *trans*, with producing only *cis* isomer. *Cis* isomer is the kinetically favored product whereas *trans* isomer is thermodynamically more stable. The *trans* isomer can be produced by converting the *cis* isomer by supplying heat energy at 180°C for time of 15 minutes. Solid phase synthesis of the *trans* isomer was also reported. Another method for synthesis of the *cis* product from copper sulphate pentahydrate was also evaluated. IR and UV spectroscopy had been used for identification purpose and also to distinguish the *cis*- and *trans*- isomers of $\text{Cu}(\text{gly})_2\cdot\text{H}_2\text{O}$.

2.1. Preparation of Complexes

Following section, enlists in brief, the procedure concerning the synthesis of *cis* and *trans* copper glycinate complexes. Syntheses had been performed in accordance with available literature protocols [25]. Note that all the main reagents were taken in stoichiometric amount excepting the solvents, and other auxiliary substances were taken in excess in Protocols 1A and 1B. All the

chemicals and solvents were purchased from SDFine chemicals and used without further purification. IR and UV spectra were recorded in Bruker ALPHA Platinum ATR FTIR spectrophotometer (direct measurement without KBr palate) and Libra BioChrom UV spectrophotometer instrument respectively. Following 4 protocols had been used for the preparation of *cis* and *trans* isomers.

2.1.1. Protocol 1A: Preparation of *cis*-bis(glycinate)copper(II)monohydrate from Copper Acetate Monohydrate [25]

Copper acetate monohydrate (2g, 10 mmol) was dissolved in 15 mL of hot distilled water (around 70°C). A hot solution of ethanol (25 mL) was added to it. Glycine (1.5g, 20mmol), previously dissolved in 10 mL hot water (around 70°C), was added to this solution and stirred, maintaining the same temperature. Overheating of the solution was prohibited. After around 5 minutes of stirring, the solution was cooled in an ice bath to form needle-like precipitate. The precipitate was filtered and washed with small portions of ethanol (3 to 4 portions of 3 mL each) and dried under vacuum and then air-dried for an hour.

2.1.2. Protocol 1B: Preparation of *cis*-bis(glycinate)copper(II)monohydrate from Copper Sulfate Pentahydrate: [26]

Copper sulfate pentahydrate (1g, 4 mmol) was dissolved in 8.5 mL of 1M HCl at room temperature and glycine powder (0.7g, 9.3 mmol) was slowly added while stirring. The solution was then kept in a water bath and its temperature was maintained at around 55°C. After 30 minutes of heating, about 1.5 – 2g of NaHCO_3 was added slowly to the solution until a blue precipitate was formed. The precipitate was washed with small portions of ethanol (3 to 4 portions of 3 mL each) and dried under vacuum and in an oven at 80°C for 10 minutes.

2.1.3. Protocol 2A: Preparation of *Trans*-bis(glycinate)copper(II) Monohydrate from the *cis* Isomer [25]

To a 20 ml portion of the filtrate obtained from Protocol 1A was added 3g (15 mmol) of the *cis* isomer (previously prepared and dried) along with 2g (26.7 mmol) of glycine powder. The solution was then refluxed at around 90°C for 1h. (An alternative method of preparation of the *trans* product would be to reflux the solution obtained in Protocol 1A prior to the filtration step at 90-100°C for 1h.) The mixture, after reflux, was allowed to cool to room temperature and then filtered with frequent washes with small portions (3 to 4 portions of 3 mL each) of ethanol.

2.1.4. Protocol 2B: Preparation of *Trans*-bis(glycinate)copper(II)monohydrate in the Solid Phase from Copper Acetate Monohydrate: [27]

A mixture of 2g (10 mmol) of copper acetate monohydrate and 2g (26.6 mmol) of glycine powder was ground using a mortar and pestle. The color of the mixture soon changed from green to pale blue. In about 1h, all the reactants were exhausted. The powder was then transferred to a watch glass and left for 2h. The completion of the reaction was indicated by a change of colour to pale blue. Small portions of ethanol (3 to 4 portions of 3 mL each) and ether (2 portions of 2 mL each) were used to wash the sample. After washing, the product was dried in vacuum.

After completion of the above 4 protocols, weigh of each product from each protocol was recorded and yield was calculated accordingly.

3. Hazard Statements

The hazard statements for the various reagents have been included in the supporting information. [14,20,21,22,28-33].

4. Evaluation of Greenness

The representative calculations of Green Star and Green Circle, done by the student as summer project, are given in the following texts. The Green Chemistry Mass Indices,

the Green Star and the Green Circle were evaluated for the four routes and the metrics are presented in Table 1. [14,15,16].

The scores and accomplishments of the principles of green chemistry are also presented below in Table 2 through 5. The reactions were not monitored with respect to the principles 4 and 11 of Green Chemistry because they were not relevant to our study. This was because the objective of the experiment was neither the real time monitoring of reactions nor was the development of lesser toxic chemicals, which precisely are conditions of the principles 4 and 11 respectively. Note that the maximum score that could be awarded for accomplishment of each principle was 3. Scores greater than 1 qualify as “Yes” in the “Accomplishment” column, while the remainder qualify for “No”.

Table 1. Tabulation of the Green Chemistry Mass Metrics, the Green Star and the Green Circle evaluated for the four preparation Routes

Protocol	1A	1B	2A	2B
E factor	29.32	14.81	9.65	6.15
MI	41.17	17.71	11.42	7.15
AE(%)	83.61	70.72	75.37	83.61
AU(%)	65.64	70.07	67.97	65.66
RME(%)	50.81	43.50	42.69	31.48
XEE(%)	77.50	73.95	82.00	62.90
Yield(%)	77.50	73.95	82.00	62.90

Green Star				
	GSAI (%)	34.44	28.89	36.67
Green Circle				

Table 2. Scores and accomplishments of the different principles of Green Chemistry evaluated for Protocol 1A

Principle no.	Description	Score	Accomplishment	Reason
P1	Prevention	1	No	Cis product is of unknown toxicity, also has wastes like copper acetate
P2	Atom Economy	3	Yes	Reaction without excess of reagents and without formation of by-products
P3	Less hazardous chemical synthesis	1	No	Cis product is of unknown toxicity, also has wastes like copper acetate
P5	Safer solvents and auxiliary substances	2	Yes	Ethanol is a hazard to the environment
P6	Increase energy efficiency	2	Yes	Heating above room temperature is required
P7	Use of renewable feedstocks	1	No	No feedstock is renewable
P8	Reduce derivatives	3	Yes	No derivatives were used
P9	Catalysts	3	Yes	No catalysts were used
P10	Design for degradation	1	No	None of the substances are degradable
P12	Safer chemistry for accident prevention	1	No	Involvement of high risk copper acetate

Table 3. Scores and accomplishments of the different principles of Green Chemistry evaluated for Protocol 1B

Principle no.	Description	Score	Accomplishment	Reason
P1	Prevention	1	No	Presence of copper sulfate
P2	Atom Economy	2	Yes	By product was sodium salt used to precipitate copper glycinate
P3	Less hazardous chemical synthesis	1	No	Involves copper sulfate and cis product of unknown toxicity
P5	Safer solvents and auxiliary substances	1	No	HCl is corrosive to the skin and may cause chemical accidents
P6	Increase energy efficiency	2	Yes	Heating to more than room temperature is required
P7	Use of renewable feedstocks	1	No	Non renewable feedstocks
P8	Reduce derivatives	3	Yes	No derivatives were used
P9	Catalysts	3	Yes	No catalysts were used
P10	Design for degradation	1	No	Waste not degradable
P12	Safer chemistry for accident prevention	1	No	Involves high risk copper sulfate

Table 4. Scores and accomplishments of the different principles of Green Chemistry evaluated for Protocol 2A

Principle no.	Description	Score	Accomplishment	Reason
P1	Prevention	1	No	Copper products are harmful to the environment
P2	Atom Economy	3	Yes	No by products were formed
P3	Less hazardous chemical synthesis	1	No	The toxicity of trans product is unknown
P5	Safer solvents and auxiliary substances	1	No	Filtrate contains moderately dangerous copper salts
P6	Increase energy efficiency	2	No	Heating and refluxing is required
P7	Use of renewable feedstocks	2	Yes	The filtrate from cis production can be used to produce trans
P8	Reduce derivatives	3	Yes	No derivatives were used
P9	Catalysts	3	Yes	No catalysts were used
P10	Design for degradation	1	No	Not degradable
P12	Safer chemistry for accident prevention	1	No	Involved unknown toxicity of product

Table 5. Scores and accomplishments of the different principles of Green Chemistry evaluated for Protocol 2B

Principle no.	Description	Score	Accomplishment	Reason
P1	Prevention	1	No	Copper products are harmful to the environment
P2	Atom Economy	3	Yes	No by products were formed
P3	Less hazardous chemical synthesis	1	No	The toxicity of trans product is unknown
P5	Safer solvents and auxiliary substances	3	Yes	It is a completely solvent free reaction
P6	Increase energy efficiency	3	Yes	Only grinding is required
P7	Use of renewable feedstocks	1	No	Feedstocks are non-renewable
P8	Reduce derivatives	3	Yes	No derivatives were used
P9	Catalysts	3	Yes	No catalysts were used
P10	Design for degradation	1	No	Not degradable
P12	Safer chemistry for accident prevention	1	No	Involved unknown toxicity of product

5. Greenness Evaluation and Comparison of the Two Routes of Synthesis of *cis*- Copper Glycinate

In the calculation of the green metrics for the *cis* product, the environmental factor (E factor) was calculated by measuring the weight of the total amount of waste generated, inclusive of the ethanol and water used to wash the samples. Thus the E factor was very high in both the protocols. Again, in the measurement of Mass Intensity (MI), water and ethanol, which were used as solvents in the reaction, were considered in the total mass of the reagents (although some calculations disregard the

mass of water, we had it involved here). Nevertheless, the greenness of the reactions were reflected by the high percentages of the indices Atom Economy (AE), Atom Utilisation (AU), Relative Mass Efficiency (RME) and Copper Element Efficiency (CuEE).

The difference in the Green Star was a clear reflection of the reagents chosen for the reaction. The high toxicity of copper sulfate pentahydrate, over copper acetate drastically affected the green star (as was evident from the scores of principles P2 and P5), and the GSAI was significantly reduced from around 34% to 29%. This was also reflected in the Green Circle, with protocol 1A had been able to accomplish 6 of the principles while protocol 1B could accomplish only 5.

Table 6. SWOT table for the two synthesis routes (Protocols 1A and 1B) of *cis* copper glycinate monohydrate

Parameters	Protocol 1A	Protocol 1B
Strengths	<ul style="list-style-type: none"> • Use of less toxic copper acetate • Less hazardous solvents like water is used • Filtrate can be reused to prepare trans product 	<ul style="list-style-type: none"> • Reaction requires not very strong heating. • High yield was observed
Weaknesses	<ul style="list-style-type: none"> • A high proportion of solvent to reagents was required 	<ul style="list-style-type: none"> • Drying at a high temperature
Opportunities	<ul style="list-style-type: none"> • The amount of solvent to be used for the reaction can be optimised upon • The yield of the product can be increased by using less solvent 	<ul style="list-style-type: none"> • Drying under vacuum can be carried out as an alternative drying process, although vacuum drying is time consuming.
Threats	-	<ul style="list-style-type: none"> • Use of highly toxic copper sulfate pentahydrate

Nevertheless, as is evident from Table 1, the protocol 1B yielded more products. A plausible reason can be, that the protocol 1A involved an excess of solvents (water and ethanol) which may have affected the yield, owing to the slight solubility of the product in the solvents. Anyway, this was a factor that could be optimized easily, and the yield via copper acetate was expected to be greater as indicated by the AE index. The SWOT table (Table 6) is presented below to give a vivid comparison between the two protocols.

6. Greenness Evaluation and Comparison of the Two Routes of Synthesis of *trans*-Copper Glycinate

The synthesis of *trans* copper glycinate via the two routes have been discussed already. The two routes were advantageous in different aspects. The Protocol 2A which dealt with synthesis of *trans* from the *cis* product, was advantageous when both the *cis* and *trans* isomers were to be prepared. The reuse of the filtrate from Protocol 1A in Protocol 2A was a major advantage. This was responsible

for the high score of Protocol 2A over Protocol 2B against the Green Principle P7.

Nevertheless, in terms of energy expenditure, Protocol 2B had an upper hand because it involved only grinding, which was done manually. Also, the reaction was a solvent free reaction, which significantly contributed to the score against Principle P5. However, the Protocol 2B has the following drawback. Owing to manual grinding, the yield may vary significantly (depending on the grinding process).

Even after repeated trials, it was observed that Protocol 2B had lesser yield than Protocol 2A.

A careful observation showed that the E factor and MI scores were significantly lower for Protocols 2A and 2B than for Protocols 1A and 1B. This was a direct consequence of the reduction in the large amounts of solvents in Protocols 2A and the solvent free synthesis route Protocol 2B. Also, the high AE value was reflective of the increased greenness of Protocol 2B. The AU values were almost equal; their differences may be attributed to experimental error. The significantly lower value of EE is due to the appreciably poor yield of Protocol 2B. Thus, despite being greener, the yield of the product was compromised in Protocol 2B. The SWOT table (Table 7) presented above provides a comparison between the two synthesis routes.

Table 7. SWOT table for the two synthesis routes (Protocols 2A and 2B) of *trans* copper glycinate monohydrate

Parameters	Protocol 1A	Protocol 1B
Strengths	<ul style="list-style-type: none"> • Reuse of filtrate from Protocol 1A 	<ul style="list-style-type: none"> • Solvent free reaction. Reaction takes place in solid phase • Energy expenditure is significantly lower than all other Protocols
Weaknesses	<ul style="list-style-type: none"> • Refluxing near boiling temperature is required 	<ul style="list-style-type: none"> • Significantly low yield. Yield may depend on the process and efficiency of grinding.
Opportunities	-	<ul style="list-style-type: none"> • Grinding process can be made more efficient to increase yield
Threats	<ul style="list-style-type: none"> • Copper salts dissolved in the waste may be harmful to the environment 	-

7. Discussions

As was evident from the table, the MI and E factor did not relate as, $E = MI - 1$. This was because of the following reasons. It was observed that the yield of the product was significantly lower than 100% and so the assumption that there was complete yield of the reaction was thought to be impractical. Also, in the Protocols 1A and 1B, a large excess of solvents was used in the reaction. Thus the waste comprised dilute solutions of copper salts. Despite being significantly less harmful to the environment, the waste of dilute copper salts was assumed to be as hazardous to the environment as the compound itself. This had resulted in a decrease in the greenness of the Protocols and hence an increase in the E factor and MI indices. Nevertheless, this could be optimized easily.

It is worth mentioning that the Green Star and hence the greenness of the above Protocols can be improved upon in ways other than those mentioned in the "Opportunities" section of the SWOT tables. Data relating to the toxicity of both the *cis* and *trans* product with respect to the various categories were either unavailable or insufficient. Also, for many of the reagents the available hazard statements dealt with only a specific category (eg. Human health, Environment and Chemical Accident). In order to combat this problem, whenever the hazard statement for one category was unavailable, the mean of the scores of the other two categories was considered. In case the hazard statement dealt with only one category, the worst score was awarded to the remaining two categories whose data was unavailable (see the hazard statement for HCl, for example). If no hazard statement was available for any

of the categories (see the hazard statements for *cis* and *trans* copper glycinate monohydrate, for example), then the worst score was awarded to each category. As an example, the “Physical Hazard” score was used to fill up the “Possibility of Chemical Accident” column, and whenever the score of the “Physical Hazard” was unavailable, the mean of the scores of hazards to “Human Health” and “Environment” was used to fill up the “Chemical Accident” column.

Noteworthy is the fact that all the reagents used in the reaction have been enlisted under the “Waste” category. The rationale behind this was that the waste contained small amounts of starting material which remained unreacted and also a small amount of the product which was lost during filtration and washing.

8. Conclusions

Green Chemistry is a matter of global concern and is achieving a matter of vital importance. With greenness of production of various chemical being encouraged in various institutions and industries, our endeavor of assessing the greenness of synthesis of copper glycinate

had been successful. In obedience to the 12 principles Green Chemistry, the assessment of the routes had been made and been critically analyzed and the results were tabulated. As mentioned already, the unavailability of data was a hindrance, thereby decreasing the greenness of the Protocols. With more data being available in future, the assessment of the Protocols mentioned may become more practical. Nevertheless, the avenues are always open for further research and study in developing a method greener than the existing ones.

9. Supporting Information

The supporting information to this paper contains the hazard statements of the various reagents used in the experiment along with IR and UV data of prepared complexes.

9.1. Hazard Statements

The Hazard Statements, compiled in accordance with the GHS for the four routes have been presented below. Note that the scores which were not available are marked as NA in the [Table 8](#).

Table 8. Hazard Statements

Reagents	Hazard Statements	Precaution Statements	Hazard to Human Health	Hazard to Environment	Possibility of Chemical Accident
Stoichiometric Reagents					
Copper acetate monohydrate	H302, H318, H410	P273, P280, P305 + P351 + P338	3	3	3
Copper sulfate pentahydrate	H301, H315, H317, H319, H334, H400, H410	P264, P270, P273, P280, P301 + P310, P302 + P352, P305 + P351 + P338, P321, P330, P332 + P313, P337 + P313, P362, P391, P405, P501	2	3	3
Glycine	NA	NA	1	NA	NA
Sodium Bicarbonate	H320	P264, P305 + P351 + P338, P337 + P313	2	NA	NA
Auxiliary Substances					
Diethyl ether	H224, H302, H316, H319, H333, H336	P210, P261, P305 + P351 + P338	2	NA	3
Solvents					
Hydrochloric Acid	H303, H314, H333, H371	P260, P264, P270, P280, P301 + P330 + P331, P303 + P361 + P353, P304 + P340, P305 + P351 + P338, P309 + P311, P310, P321, P363, P405, P501	3	NA	NA
Ethanol	H303, H225, H315 + H320, H333, H335, H401	P210, P261, P305 + P351 + P338	2	3	3
Water	None	None	1	1	1
Products formed					
Cis Copper glycinate monohydrate	NA	NA	NA	NA	NA
Trans Copper glycinate monohydrate	NA	NA	NA	NA	NA
Wastes produced					
Copper acetate monohydrate	H302, H318, H410	P273, P280, P305 + P351 + P338	3	3	3
Copper sulfate pentahydrate	H301, H315, H317, H319, H334, H400, H410	P264, P270, P273, P280, P301 + P310, P302 + P352, P305 + P351 + P338, P321, P330, P332 + P313, P337 + P313, P362, P391, P405, P501	2	3	3
Glycine	NA	NA	1	NA	NA
Sodium Bicarbonate	H320	P264, P305 + P351 + P338, P337 + P313	2	NA	NA
Hydrochloric Acid	H303, H314, H333, H371	P260, P264, P270, P280, P301 + P330 + P331, P303 + P361 + P353, P304 + P340, P305 + P351 + P338, P309 + P311, P310, P321, P363, P405, P501	3	NA	NA
Ethanol	H303, H225, H315 + H320, H333, H335, H401	P210, P261, P305 + P351 + P338	2	3	3
Water	None	None	1	1	1
Diethyl ether	H224, H302, H316, H319, H333, H336	P210, P261, P305 + P351 + P338	2	NA	3
Cis Copper glycinate monohydrate	NA	NA	NA	NA	NA
Trans Copper glycinate monohydrate	NA	NA	NA	NA	NA

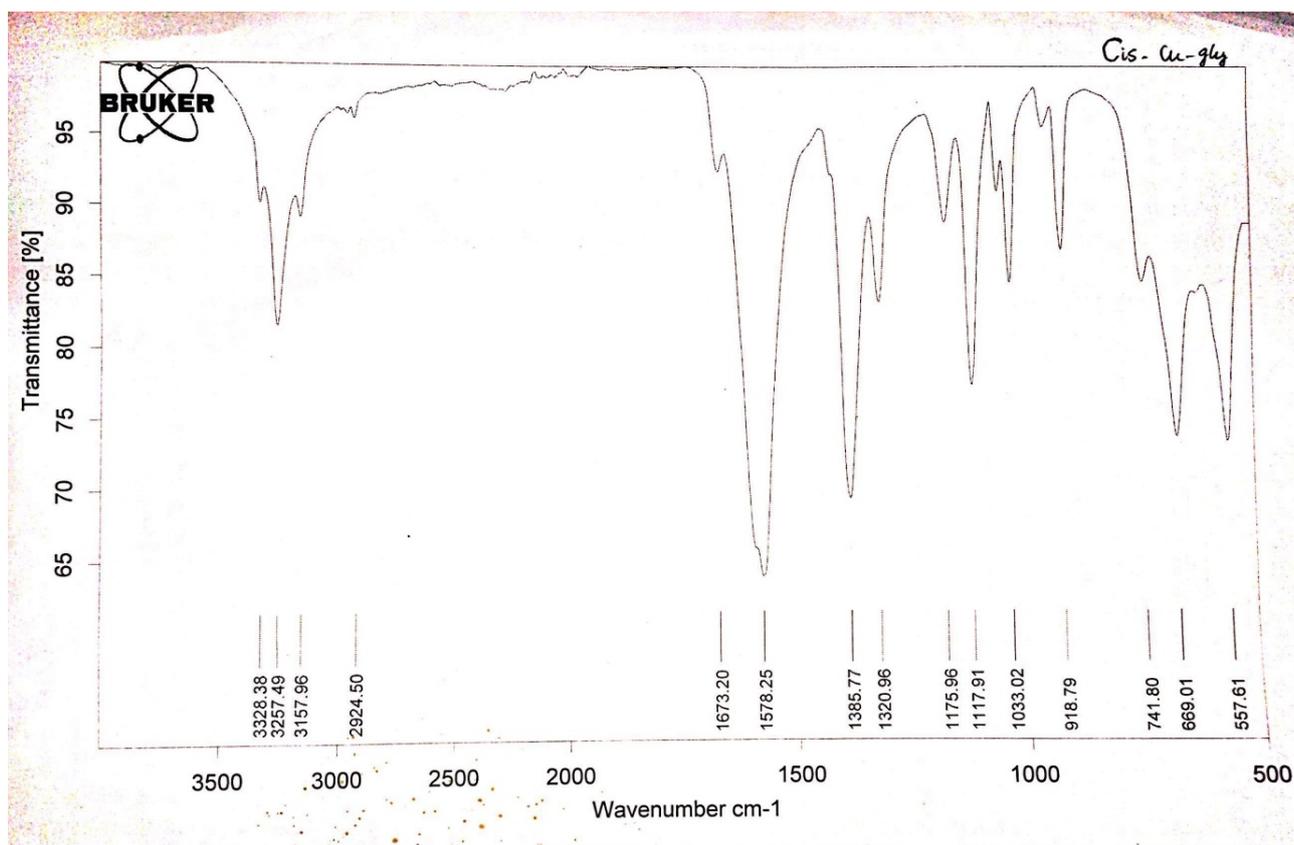


Figure 1. IR Spectra of *cis*-bis(glycenato)copper (II) monohydrate complex: (Measured in ALPHA Bruker PlatinumATR FTIR spectrophotometer)

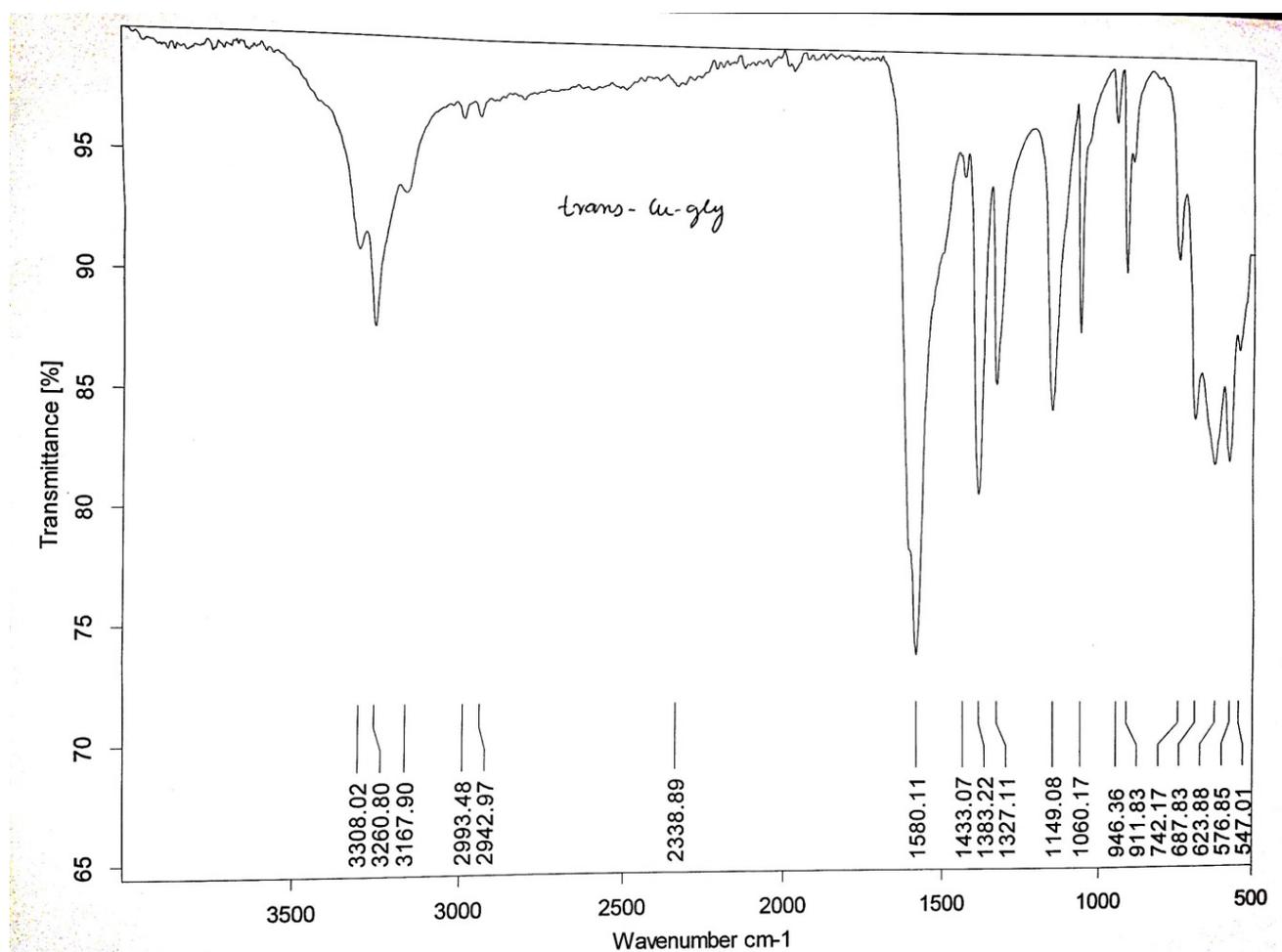


Figure 2. IR Spectra of *trans*-bis(glycenato)copper (II) monohydrate complex: (Measured in ALPHA Bruker PlatinumATR FTIR spectrophotometer)

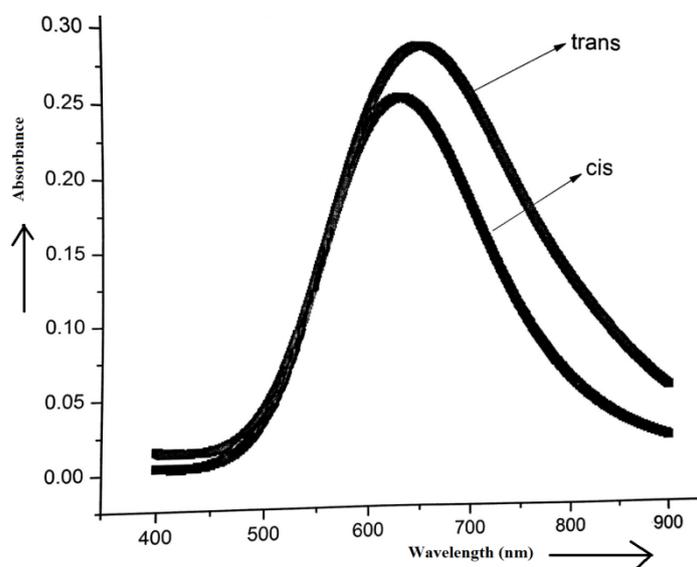


Figure 3. UV spectra of cis and trans complexes: (measured in Libra BioChrom UV spectrophotometer)

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