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Synthesis and Characterization of Chromium (III) Complexes with L-Glutamic Acid, Glycine and L-Cysteine

Kun Sri Budiasih, Chairil Anwar, Sri Juari Santosa, and Hilda Ismail

Abstract**—**Some Chromium (III) complexes were synthesized with three amino acids: L Glutamic Acid, Glycine, and L-cysteine as the ligands, in order to provide a new supplement containing Cr(III) for patients with type 2 diabetes mellitus. The complexes have been prepared by refluxing a mixture of Chromium(III) chloride in aqueous solution with L-glutamic acid, Glycine, and L-cysteine after pH adjustment by sodium hydroxide. These complexes were characterized by Infrared and Uv-Vis spectrophotometer and Elemental analyzer. The product yields of four products were 87.50 and 56.76% for Cr-Glu complexes, 46.70% for Cr-Gly complex and 40.08% for Cr-Cys complex respectively. The predicted structure of the complexes are $[Cr(glu)_2(H_2O)_2].xH_2O$, $Cr(gly)_3.xH_2O$ and $Cr(cys)_3.xH_2O$, respectively.

Keywords**—**Cr(III), L-Cysteine L-glutamic Acid, Glycine, complexation.

I. Introduction

CHROMIUM(III) is a trace mineral which is needed as supplement in management of diabetes mellitus. It has an important role in glucose metabolism.

Biological function of chromium is not fully known yet. The diabetes relevant interaction of Cr (III) is with the hormone insulin and its receptors. This suggests that Cr (III) acts with insulin on the first step in the metabolism of sugar entry into the cell, and facilitates the interaction of insulin with its receptor and the cell surface [1], [2]. Chromium increases insulin binding to cells, insulin receptor number and activates insulin receptor kinase leading to increased insulin sensitivity [3].

The most popular chromium supplement is Chromium picolinate, $Cr(pic)_3$, a relatively well absorbed form of chromium (III). The disadvantage of $Cr(pic)_3$ is the effect of this compound in DNA damage[4]. Comparative studies of chromium(III) picolinate and niacin-bound chromium(III), two popular dietary supplements, reveal that chromium(III) picolinate produces significantly more oxidative stress and DNA damage. Administration of the supplement to rats has demonstrated for the first time that it can give rise to oxidative DNA damage in whole animals [5]. The search for compounds with novel properties to deal with the disease condition is still in progress.

Another form of Cr(III) supplement is Chromium ascorbate complex [6].There is a direct relationship between the charge of the Cr(III) species and their reactivity with DNA. The positively-charged complexes displayed ultimate DNA-breaking properties, while the neutral and negatively-charged complexes were almost inert. Yang [7] proposed D-phenylalanine, an amino acid, as a novel ligand for Chromium (III) complex. The product was $Cr(pa)_3$. Unlike chromium picolinate, $Cr(pa)_3$ does not cleave DNA under physiological conditions.

Some amino acids with Cr(III) have been reported as a part of GTF (*Glucose Tolerance Factor*), a molecule, that is, involved in the function of insulin in the processing of glucose into energy. It is an oligopeptide of molecular weight about 1438, and composed of glycine, cysteine, aspartate and glutamate with the acidic amino acid comprising more than half. One mole of this compound binds four molecule of Cr(III) very tightly. This manifests as the hormonal action of insulin. Natural GTF is a fraction isolated from brewer's yeast which plays a biological activity in glucose metabolism [8]. The similar study also published that a solution which contains chromium (III), glycine, glutamic acid and cystein mimics the biological activity of the naturally occurring GTF [9]. Another study reported the relationship between chromium(III) -amino acids complexes with GTF activity using a yeast assay[10].

Unfortunately, the research on the synthesis of chromium complexes with amino acids is not well developed. Some problems found from these research on this topic. Several works in this topic reported rarely from the 70's to90's and did not be continued and did not related to one another. The subsequent report appeared in the 2000s.

One of the commonly cited for the synthesis of complexes of Chromium with amino acid ligands is the procedure of Bryan [11]. However, Wallace [12] reported that the synthesis methods are not reproducible. Many trials are needed to get a consistent product from a particular procedure.

Some works also reported different products from the same raw materials. The reasons are due to differences in the reaction conditions [13], the possibility of many products [14]-[16] and formation of geometric isomers [17]. The difficulties

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of synthesis especially found in glycine and cysteine complexes [18], [19].

Another problem is also encountered when referring to the procedure of Cr-amino acid synthesis. For example, Yang [7] explained the simple method of synthesis of Cr-phenylalanine by mixing $CrCl_3.6H_2O$ and D-phenylalanine in water, and refluxed at 80°C for 4h. However, applying this procedure did not give the appropriate result.

Based on these facts, further studies on the synthesis and characterization of Cr(III)-amino acid complexes is still needed. Some modification applied to the previous procedure. This is necessary in order to obtain a definitive and reproducible method and consistent product, which will be applied in vivo as an antihyperglycemic supplement.

II. Experimental Section

A. Materials

Chromium (III) chloride hexahydrates ($CrCl_3.6H_2O$) salts, and amino acids: L- Glutamic Acid (Glu), Glycine (Gly), and L-cysteine (Cys) were of Laboratory grade (by E-Merck) and used as such without purification. Sodium hydroxide (E-Merck) was used to adjust the pH.

B. Preparation of the Complexes

The Cr(III) complexes of L-Glutamic Acid ligand were prepared in 1:3 and 1:2 [metal:ligand] ratio. To a 50ml water solution of Chromium (III) chloride (0.26g, 1mmol), NaOH 0.1M was added to adjust the pH. The ligand solution of Glutamic acid then was added (3mmol or 2mmol) to obtain 1:3 and 1:2 ratio. The resulting mixture was stirred under reflux for 1h and 80°C.The precipitated product was collected by Buchner filtration, washed with water, and dried in air. This method was based on the experiment of Yang [7] with some modification in pH adjustment and the sequence of the process. The yielding solid was weighing until constant weight.

The glycinato complex of Cr(III) was synthesized based on modified Bryan's procedure [11].The complex was prepared by refluxing the aqueous solution of ($CrCl_3.6H_2O$), glycine and NaOH in the molar ratio 1:3:3 for 3 hours.

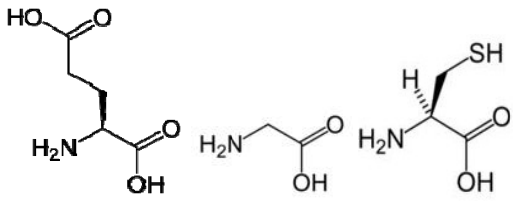
The Cr(III)-cysteine complex was prepared by the same procedure of Cr(III)-glutamic acid complex.

C. Characterization and Measurement

The resulting complexes in this work were characterized by physical properties by observation of the solid performance and the color of the precipitation. The yield was determined by weighing the product and compared with the starting materials. Infra red spectra were recorded on Shimadzu FT-IR 8300 spectrophotometer from at 4000-400cm^{-1} using KBr pellet technique. The UV-Vis spectra were studied in HNO_3solvent with concentration about 1% b/v by UV Vis spectrometer (Thermo Spectronic), with 1cm^2 quartz cell within the range of 360-650nm. Elemental Analysis was carried out at Faculty of Food Science and Technology, University Kebangsaan Malaysia.

III. Result and Discussion

The structure of L-glutamic acid, glycine and L-Cysteine was shown at Fig. 1.



(a) (b) (c)

Fig. 1 (a) L-Glutamic Acid, (b) Glycine, and (c) Cysteine

Formation of the Cr(III) complexes was achieved by reaction of the ligand with Cr (III) salts by reflux method. Color changes at the flask indicate the occurrence of reaction. The complex formation observed in various pH according to the concentration of Cr^{3+} ion in water solution which influenced by pH. The highest concentration of Cr^{3+} is reached at pH 4,0- 4,5. Solution of $CrCl_3.6H_2O$ was adjusted to pH=4 before mixing with the amino acid ligands. Complexes from samples of pH 2,5 and 3 were not obtained [20].

Products yield and physical data are presented in Table I.

TABLE I
Product Yield of the Cr Complexes

Complex	M:L ratio	Product and physical data	
		color	Yield (%)
Cr (III) – glutamic acid	1:3	Purple	87.50
Cr (III) – glutamic acid	1:2	purple	56.76
Cr (III) – glycine	1:3	Bluish purple	46.70
Cr (III) – cysteine	1:3	Deep purple	40.08

FTIR spectra of these products were shown in Figs.2, 3, and 4 and listed in Table II. The IR spectra in 4000-400cm^{-1} region show the evidence of complex formation. They were analyzed by comparison with data of the free ligands. Generally, free amino acid have original peaks of stretching vibration of ammonium and carboxylate groups in the broad region of 2600 and 1600cm^{-1}, respectively [21].

The Infrared spectra of Cr with glutamic acid were shown at Fig. 2. Comparison of the infrared spectral data of complexes and the ligand confirmed that complex formation has occurred as significant shifts in the bands of the OH groups were observed in the region 3000-3500cm^{-1}. The IR spectra of Cr(III) complexes showed the expected characteristic ν_{as} COO^- band in the region of 1512.19$cm^{-1}$is disappeared due to metal coordination. Park [16] previously reported the similar bands at 1156-158 cm^{-1}.

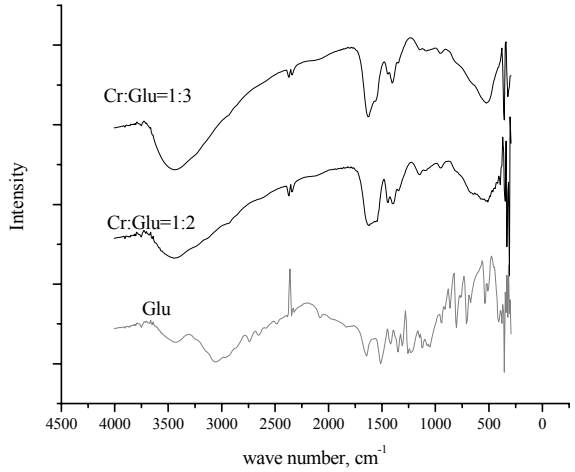


Fig. 2 FTIR spectra of Cr-Glu complex

A sharp band at 1643.35cm^{-1} in the ligand due to C=O vibration was also shifted to lower frequency (1620.21-1604.77) in the complexes. Moreover, the appearance of additional weak bands in the region 401-447 and 540.07-532.35cm^{-1} which were attributed to $\nu_{(Cr-O)}$ and $\nu_{(Cr-N)}$, respectively, confirmed the complexation.

Infrared spectrum confirmed the formation of the complex by m-C-O (1563cm^{-1}) and m-N–H (3535cm^{-1}) and the band shifting by about 40 and 30cm^{-1} respectively. The moderately sharp absorption band in the free ligand (3000–3500cm^{-1}) was shifted to about 600cm^{-1} may be related to the reorganization in intramolecular hydrogen bonding after the formation of chelating complex. New absorption bands in the far IR region around 385-410cm^{-1}, 324-337cm^{-1}, and 447.49cm^{-1}- 424,34cm^{-1} can be assigned to the Cr–O and Cr–N bonds. It is match with previous study that reported these bands at390cm^{-1}, 330cm^{-1}, and 542-525cm^{-1} [21]. Coordination bond in Cr-glu complex was predicted occurred through the COOH group. It was indicated from the disappearance of 1660cm^{-1} band from glutamic acid [14].

Infrared spectra of complexation of Cr(III) with glycine was shown at Fig.3.

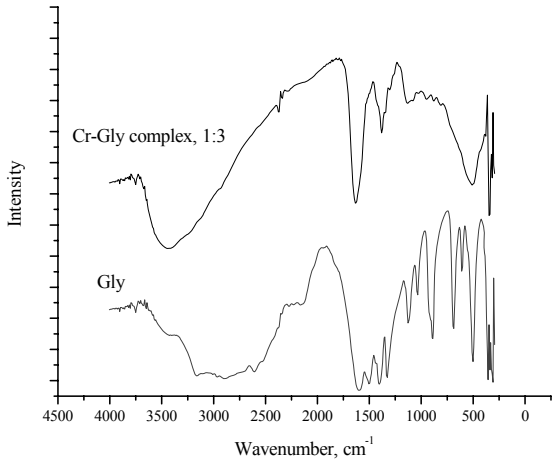


Fig. 3 FTIR spectra of Cr-Gly complex

There are some significant differences of FTIR pattern of Cr-Glycine complex with the free ligand. The shift to lower wave number from 1404.18cm^{-1} (Gly) to 1381.03cm^{-1} (Cr-Gly complex) corresponds to the symmetric vibration of COO^-. A study of $Cr(Gly)_3$ complex formation reported this shift by 1400-1370cm^{-1}[19]. A recent publication explained that the N-H stretching vibration at 3109cm^{-1} in glycine was shifted to higher frequencies (3333-3428cm^{-1}) in the complex, suggesting that the coordination of the metal ion (in this case, Cu, Cd, Ni, Co, Mn) with the ligand was via the nitrogen atom. Shifting of C-N stretching 1127 to (1210-1236cm^{-1}) also support this idea [24]. In this work, the N-H stretching vibration was shifted from 3109.25cm^{-1} to 3425.58cm^{-1} and the C-N stretching vibration shifted from 1126.43cm^{-1} to 1303.88cm^{-1}

The Infrared spectrum of Cr with cysteine was shown at Fig. 4.

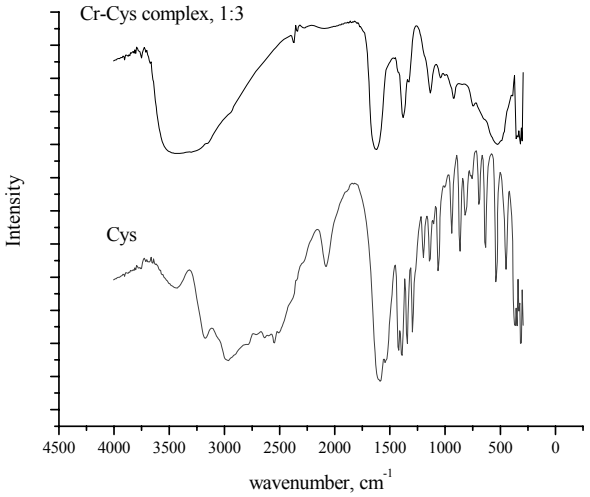


Fig. 4 FTIR spectra of Cr-Cys complex

The Infrared spectra of cysteine complex show several significant bands. The asymmetric stretching band of COO^- shifted to higher from 1589 to 1620cm^{-1}, indicating that the carboxylate group was involved in the coordination. A previous study also reported a similar shift of wave number by 20-70cm^{-1}, from 590 to 1640cm^{-1}[22]

Asymmetric stretching of NH_2 were shifted to lower wave number after formation of coordination bond with Cr. Cr-N vibrations were shifted from 1543 and 1064cm^{-1} to 1620 and 1381cm^{-1} respectively. According to El-Shahawi [22], it confirming the participation of the nitrogen atom of the amino group of cysteine in the coordination with Cr(III), with the shifting from 1505-1540cm^{-1} and 1120cm^{-1} to 1570-1580cm^{1} and 1200cm^{-1}.

These spectra showed a clear pattern which shows the difference between the produced complex with their free ligands. The characteristic absorption in the IR spectra of complexes is listed in Table II. The data from the reference(s) were placed in square brackets.

TABLE II
INFRARED VIBRATION OF THE COMPLEXES AND THEIR LIGANDS

Vibration	Cr-Glu (I)	Cr-Glu (II)	Glu	Cr-Gly	Gly	Cr-Cys	Cys	Reference(s)
υC=O	1604.77	1620.21	1643.35	1635.64	1604.77	1620.21	1589.34	[21]
υ_{as} COO^-	-	1558.48	1512.19		1504.48		1543.05	
υ_s COO^-	1404.18	1396.46	1419,61	1361.03	1404.18	1381.03	1420.05	
δ COH	-		1257,59				1296.16	
υ C-O	1149.57	1149.57	1126.73;1257.59 [1150]		1126.43	1134.14	1141.86 1195.87	
δ CH_2	1442.75;1450.47	1442.75	1419,61 [1440]	-	[1441-1446]		[1424-1432]	[21]
δ C-H	1342.46	1342.46	1311.59 1125		[1333-1337]		[1341]	[21]
υ N-C	-	-	1257.59					
Υ_t CH_2, δ CH	-	-	1226.73		[1310-1315]		[1303, 1297]	[21]
υ C-C	1087.85; 1049.28	1095.57	1075 1056.99	1134.14	1033.85	1134.14	1064.71	
υN-H	3425.48	3448.72	3062.96	3425.58 [3333-3428]	3109.25 [3119]	3302.13	3170.91	[23]
υS-H	-	-	-	-	-	-	[2551]	[20]
Cr-$O_{stretch}$	540.07	509.21	-		-		-	
Cr-O strech	347.19 [337, 393]	347.19			-		-	
Cr-O	424.34 [413] [442]	-			-		-	[16]
Cr-N	478.35	509.21	-		-	[1064] [1381]		

υ = stretching; υ_s = symmetric stretching; υ_{as} = asymmetric stretching; w = weak intensity; Υ_t = twisting; Υ_w = wagging; Υ_r = rocking. Ref: [19]-[22].

Uv-Vis Spectrometric spectra of the complexes were shown at Fig. 5.

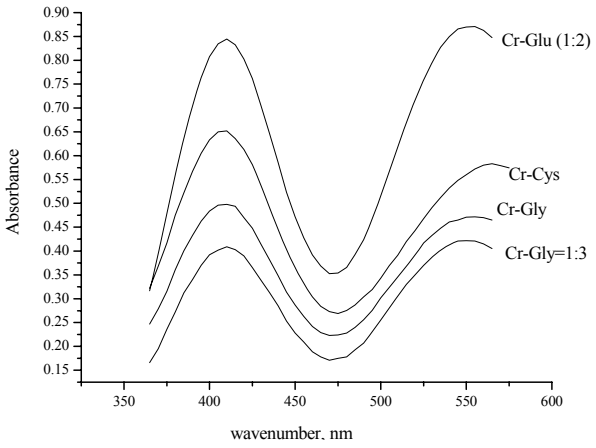


Fig. 5The UV-Vis spectra of Cr complexes

The coordination of metal to ligands caused a certain change in electronic configuration of the d-orbitals. Complexes of transition metal with electronic absorbtion at the visible light, the coordination formation is related to the color change, due the change of electronic configuration [23]. In the case of Cr(III), all samples showed color changes from the solution of metal ion and the ligand to a new color of complex. It is correspond to the d^3-electronic configuration of Cr^{3+}. Enhancement of Uv-Vis absorption in the range of 350-570 nm was observed to all Cr complexes in this work. The characteristic maximum absorption is at about 410nm and 560nm.

A previous study reported the maximum absorbtion of $[Cr(gly)_2]^-$ is at λ_1=548nm and λ_2=420nm [17]. Complex of Cr(Gly)3 showed two peaks at 386 and 510 respectively, when the $[Cr(gly)_2(OH)]_2$ have maximum absorption at 403 and 535nm [18].

The elemental analysis data are given in Table III.

TABLE III
RESULT OF ELEMENTAL ANALYSIS OF THE COMPLEXES

Complexes	%C	%H	%N
Cr (III) – glutamic acid, 1:3	19.695	7.542	7.303
Cr (III) – glutamic acid; 1;2	20.965	6.602	6.478
Cr (III) – glycine, 1:3	11.047	5.493	5.704
Cr (III) – cysteine, 1:3	12.385	6.492	5.637

Calculation of the result gives the prediction of $_{the}$ ratio of each element in the complexes. The amount of oxygen was calculated from total 100% constituent. Two complexes of Chromium with glutamate have a similar ratio. The excess of hydrogen and oxygen indicates that there are some water molecules in the complexes.

There are some possible formulas of Cr-L glutamic acid, Cr-Glycine and Cr-cysteine complexes. According to Rasuljan [14], the tris complexes of glutamic acid were synthesized from Cr(III) nitrate at pH 6-7. The products were $Cr(glu)_3.2H_2O$ (pink) and $Cr(glu)2OH.4H_2O$ (pink). Reaction at pH 7.5 from 1;2 metal ligand ratio produced compounds containing one hydroxyl group and two molecule of glutamic acid. The resulting compounds were $Cr(glu)_2OH.5H_2O$(blue) and $Cr(glu)_2OH.6H_2O$(purple). Four other compounds are $[Cr(glu)(OH)_2]2$, pink; $[Cr(glu)(OH)_2]H_2O$, grey blue; $[Cr(glu)(OH)_2]2H_2O$, grey blue, and $[Cr(glu)(OH)_2]3$ H_2O, blue. They were containing 2 hydroxyl groups and 1 glutamic acid and produced by metal ligand ratio of 1;1 at pH=8.

All these products were produced at higher pH value (6-8). In the condition, the complexes produced in this system containing hydroxyl group(s) because of the high

concentration of OH^-. In the same time, a higher possibility of $Cr(OH)_3$ precipitation, which can show an O-H signal in infrared spectra.

Meanwhile, all the complexes produced in this work were conducted at pH under 4, 5 when the concentration of hydroxide ions was quite low. So, the predicted structure is not the same as the Rasuljan's work.

El-Megharbel [25] reported the structure of three metal ions (Mn^{II}, Cr^{III}, and Fe^{III})-methionine complexes. . There is no significant peak at 3450cm^{-1} region of FTIR spectra so there is no water molecule in the complexes as coordinated water or as water of crystallization. The most possible structure are ML_2 for Mn and ML_3 for Cr and Fe. Two weak bands at 3422cm^{-1} and 3419cm^{-1} in Cr(III) and Fe(III) complexes respectively is claimed as the bands of O-H vibration by moisture at the sample.

An additional experiment of the two Chromium(III)-glutamic acid complexes in this work was conducted to determine the existence of water. After heating at 80^{o}C there was a color change from purple to grey, due to the water loss. Water existence as the coordinated part or as crystallized water was not known yet. Both complexes of 1:3 and 1:2 ratio (Cr:Glu) show the same phenomena. Therefore, the structure of both glutamic complexes is presumed identical. $[Cr(glu)_2(H_2O)_2].xH_2O$ is the probable structure of these complexes if there are water molecules act as coordinated molecule and also as crystallized water. Other probable structure is $Cr(Glu)_3$ if water loss is due to the crystallized water or the presence of moisture, according to the analog complex of Cr(III) with methionine in El-Megharbel's work.

The predicted structure of Cr-Gly and Cr-Cys complexes are $Cr(gly)_3.xH_2O$and $Cr(cys)_3.xH_2O$ respectively.

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