Synthesis and characterization schiff base

by Fatma Fatma

Submission date: 05-Jun-2023 11:22AM (UTC+0700)
Submission ID: 2109147390
File name: Synthesis_and_characterization_schiff_base.pdf (1.03M)
Word count: 2805
Character count: 14770

Synthesis and characterization schiff base and complexes with Copper (II) and Iron (II) and their application as antibacterial agents

IOP Conf. Series: Journal of Physics: Conf. Series **1282** (2019) 012074 doi:10.1088/1742-6596/1282/1/012074

Synthesis and characterization schiff base and complexes with Copper (II) and Iron (II) and their application as antibacterial agents

N Hidayati, Fatma, and W Purwaningrum

Departement of Chemistry Faculty of Mathematics and Natural Sciences University of Sriwijaya, Jalan Raya Palembang Prabumulih Km 32 Indralaya, Ogan Ilir 30661

E-mail: hidayatinurlisa@yahoo.com

Abstract. The Schiff base N-(2-hydroxybenzylidene)chitosan and its complexes with copper(II) and iron(II) were synthesized and applied as antibacterial agent. The Schiff base and its complexes characterized by UV-Vis, FTIR spectrophotometer and XRD diffractometer. Antibacterial activity of the Schiff base and its complexes toward *Escherichia coli and Staphylococcus aureus* bacteria were assessed by paper disc diffusion method. Electronic transition indicated the absorption of azomethine group from Schiff Base and absorption of d-d transition from metal ion. FTIR characterization of Schiff base indicated the azomethine group have been formed. Absorption Schiff base shifted indicating coordinated to metal ion. X-ray diffractometer studies show the formation of complexes decreased of cristalinity of chitosan. The complexes of copper(II) and iron(II) with N-(2-hydroxybenzylidene)chitosan have antibacterial activities bigger than the Schiff Base or pure chitosan attributed to the increased lipophilic nature of the complexes arising due to chelation.

1. Introduction

During last few years Schiff base compound become one of hot interests because their interesting or useful properties. Chitosan Schiff bases have binding ability to heavy metal ion formed complex compound by chelation. These complexes uses for a large activities such as catalyst, antimicrobial agent, antioxidant and antibacterial agent therefore studies on complex Schiff base with numerous metal ion has been reported [1-4]. Interestingly, most of research about Schiff base modified chitosan–metal ion only focus on their application as catalyst. Copper, cobalt and nickel complexes of Schiff modified chitosan was reported have catalitic activity in cyclohexane oxidation. Research about application complexes of Schiff modified chitosan as antibacterial agent only few available.

Chitosan (poly-β-(1→4)-glucosamine) is a abundance non toxic natural biopolymer. It is derived from deacetylation of chitin, natural polysaccaride that is usually obtained from shell of crustaceans such as crab, shrimps, crawfish. Chitosan is a biocompatible, biodegradable and non toxic natural biopolymer which its applications ranging from cosmetics, artificial skins, photography, food and nutrition, ophthalmology and wastewater treatment [5-9].

Chitosan contains amine and hydroxy group which under mild reaction condition can be used to chemically alt its properties. Amino group of chitosan can be reacted with aldehyde or ketone form Schiff Base. Schiff base compounds containing an azomethine or imine group (-RC=N-), are synthesized by nucleophilic addition or condensation of primary amine and carbonyl group. Schiff

bases which containing various donor atoms can act as chelating ligand and react with metal ion [1,8,9].

The present work describes the preparation of Schiff Base through reaction between chitosan with 2-hydroxybenzaldehyde. The Schiff Base then reacted with Cu(II) and Fe(II) to form complex compound. The characterization of products have been formed by spectroscopy UV-Vis, FTIR and XRD. Antibacterial activities of the product against *E.coli* and *S.aureus*.

2. Experimental Section

2.1. Materials

Chitosan was purchased from CV. Bio Chitosan Indonesia with the degree of deacetylation was 87.5%. Glacial acetic acid, 2-hydroxybenzaldehyde, dimethylsulfoxide (DMSO), methanol, ethyl alcohol (96%), $CuSO_4.5H_2O$ and $Fe(SO_4).7H_2O$ all in analytical grade were purchased from Merck. *E.coli* and *S.aureus* were supplied by Microbiology Laboratory, Department of Biology, Faculty of Mathematic and the Natural Sciences University of Sriwijaya.

2.2. Instrumentation

The instruments used for characterization included UV-Vis Spectrophotometer (Shimadzu 1420 Mini) for identify electronic transition. Fourier Transform Infrared (FTIR) Spectrometer (Shimadzu 8201) was used for identify the presence of functional groups. X-ray powder diffraction determinations were accomplished using X-ray diffractometer (Shimadzu XRD-6000).

2.3. Procedure

2.3.1. Synthesis The Schiff Base N-(2-hydroxybenzylidene)chitosan. An 800 mg chitosan dissolved in 50 mL acetic acid 0.1 mgL^{-1} and stirred for 30 min at room temperature. A 4 mL 2-hydroxybenzaldehyde dissolved in 20 mL ethanol previously and then added to chitosan solution. The mixture was refluxed with stirring at 60^0C for 12 h. After the cooling product was filtered and the unreacted aldehydes were washed using ethanol. The product was dried at 60^0C for 24 h.

2.3.2. Synthesis Complexes N-(2-hydroxybenzylidene)chitosan with Cu(II) and Fe(II). Each a 400 mg N-(2-hydroxybenzylidene)chitosan dissolved in 10 mL DMSO. The solution then added 10 mL Cu(II) 0.1 mgL^{-1} and 10 mL Fe(II) 0.1 mgL^{-1} respectively then refluxed at 60^oC for 12 h. After cooling, the mixture was filtered. The complexes compound yielded was washed with ethanol and dried at 60^oC.

2.4. Characterization of N-(2-hydroxybenzylidene)chitosan and its Cu(II),Fe(II) complexes.

2.4.1. FTIR spectroscopy. The infrared spectra were recorded on a Shimadzu 8201 FTIR spectrophotometer using KBr pellet at room temperature. The spectrum was recorded within the wave number range 400-4000 cm^{-1}.

2.4.2. UV-Vis Spectroscopy. UV-Vis absorption spectra of the N-(2-hydroxybenzylidene)chitosan and its Cu(II),Fe(II) complexes were recorded on spectrofotometer with a scan range 200-800 nm. All samples were diluted 0.1 mgL^{-1} acetic acid as solvent.

2.4.3. XRD Diffraction. XRD analysis of N-(2-hydroxybenzylidene)chitosan and their complexes with Cu(II) and Fe(II) were performed in the 2θ range from 5^o to 80^o.

2.5. Antibacterial assay

Antibacterial activities were investigated using paper disc method. The activity of tested samples was studied againts the *S.aureus* (as gram-negative bacteria) and *E.coli* (as gram positive bacteria). The bacteria were cultured in 12 mL nutrient agar medium in sterilized petri dish (12 mm diameter). The complex in various concentration poured over discs (6 mm diameter) and placed over on the top of

agar layer. The discs were incubated at 37^{0}C for 24 hours. The zone of inhibition of growth was measured, which indicated the inhibitory activities of the compound. The average of three diameter was calculated for each sample. The antibacterial activities also investigated for chitosan and N-(2-hydroxybenzylidene)chitosan.

3. Results and Discusion

3.1. Identification Electronic transition by UV Vis Spectrophotometer

A schematic ilustration of the complexation between Schiff Base and ion metal is depicted in figure 1. Electronic spectra of Schiff Base N-(2-hydroxybenzylidene) chitosan (abbreviated as CSB) and their complex compounds namely CSB-Cu(II) and CSB-Fe(II) obtained by spectrofotometer at wavelenghth range 200-800 nm. Figure 2 represented electronic spectra of CSB, CSB-Cu(II) and CSB-Fe(II). Absorptions at around 320 nm were an electronic transition from n→π* of an azomethin group of Schiff base derived from the reaction between chitosan and 2-hydroxybenzaldehyde [10,11].

Electronic spectra of Schiff base complexes with Cu(II) and Fe(II) showed an absorption maximum above 400 nm due to d-d transitions derived from metal ions. Absorption at 458 nm and 455 nm corresponds to the d-d electron excitation of Cu(II) and Fe(II). This band observed to be quite weak because transitions would theoretically be forbidden by Laporte rule. The copper (II) ion and iron (II) ion in aqueous solution have absorption maximum at 810 and 1020 nm respectively [12]. This result indicated that absorption maximum of Cu(II) and Fe(II) in shifting to a lower wavelength due to complexation. Chelating formation between Schiff base and Cu(II) or Fe(II) resulting a more stonger binding therefore splitting parameter (Δo) of d electron became larger. The more larger splitting parameter more bigger the energy of absorbed light and more lower the wavelength.

Table 1. electronic transition of CSB, CSB-Cu(II) and CSB-Fe(II)

Compound	Absorption (λ_{maks}) (nm)	
	d-d	n→π* azomethine
CSB	-	323
CSB-Fe(II)	458	320
CSB-Cu(II)	455	325

3.2. Identification of functional group by FT-IR

A broad absorption band which corresponds to stretching vibrations of O-H and N-H functional group from chitosan observed at approximately 3400 cm^{-1}. Streching bands due to skeletal vibration of C-O occur at 1037 cm^{-1}. Absorption of β-(1→4) glycoside bridge which characterized chitosan saccharide structure is noted at 1158 cm^{-1} and 892 cm^{-1} [2]. These significant bands which characterized chitosan are expected presence in CSB and its complexes.

The FT-IR spectra of CSB, CSB-Cu(II) and CSB-Fe(II) are shown at Figure 3. The broad absorption band which corresponds to streching vibration O-H and N-H which derived from CSB can be observed at wave number 3448.7cm^{-1}. Absorption band observed at 2885.5 cm^{-1} and 2924.1 cm^{-1} due to the C-H vibration stretch of –CH_2 group. Streching vibration of C-O-C from CSB can be observed at 1033.85 whereas for CSB- Fe(II) and CSB- Cu(II) at 1018.4 cm^{-1} [2,13, 14, 15]. The functional group of O-H stretching vibration of CSB appeared at wavenumber 3448.7 cm^{-1}. This band has been shifted to shorter wavenumber at 3433.3 cm^{-1} for CSB- Cu(II) and 3425.6 cm^{-1} for CSB-Fe(II) respectively indicating coordination between the metal ion and Schiff base through hydroxy functional group. The formation of coordination bond between M and azomethine is confirmed by absorption at 393.48 cm^{-1} due to vibration of M-N [16]. Absorption at wavenumber 300-600 cm^{-1} indicating that complex compound has formed.

3.3. X-ray diffraction analysis

The Crystallinity of chitosan, chitosan Schiff base (CSB) and their complexes with Cu(II) and Cu(II) were investigated by XRD. The x-ray diffraction pattern of chitosan and its derivative compound had characteristic peak around 20°[2]. Figure 4 shows diffraction pattern of chitosan, CSB and their complexes. The characteristic peak of CSB, CSB-Fe(II) and CSB-Cu(II) at 2θ =~20° are much wider and weaker than chitosan.This result indicates that cristallinity of CSB, CSB-Fe(II) and CSB-Cu(II) decreased compared to chitosan due to deformation of strong intramolecular hydrogen bonding in the chitosan backbone was caused by azomethine formation.

3.4. Biologial studies

The antimicrobial activities of CSB, CSB-Fe(II) and CSB- Cu(II) were screened againts *E.coli* and *S.aureus* bacteria. Result of bacterial screening are summarized at Table 2. The bacterial screening results showed that complex compound of CSB have higher activites than chitosan and CSB. This attributed to to the increased lipophilic nature of the complexes arising due to chelation. The enhanced activity of the metal complexes is probably due to faster diffusion of the chelates as a whole through the cell membrane or due to the chelation theory [6]. Metal ion-CBS chelates will increase the positive charge density of chitosan and inturn enhance inhibition activities

The antibacterial activities of CSB-Cu(II) were higher than that of CSB-Fe(II). Interaction between Copper (II) with CSB is stronger because Cu (II) has smaller radius and more extra nuclear electron than Fe(II) based on Irving-William Series. Cu (II) will posses stronger interaction with CSB so complex CSB-Cu(II) is easy to bind with cell surface of bactery and antibacterial activities will increase. [17]

Table 2. Diameter of zone of inhibition of N-(2-hydroxybenzylidene)chitosan and their complexe compounds

Compound	concentration (ppm)	Diameter of zone of inhibition (mm)	
		E.coli	*S.aureus*
Chitosan	0	0	0
	125	6	6
	250	6	6
	500	7	8
	1000	8.75	9.25
CSB	0	0	0
	125	6	6
	250	6	6
	500	7.6	6
	1000	9.5	9.33
CSB- Cu(II)	0	0	0
	125	6	6
	250	7	7
	500	8	8
	1000	10.67	11.58
CSB-Fe(II)	0	0	0
	125	6	6
	250	6	6
	500	7	7
	1000	9.86	10.16

4. Conclusions

Schiff base derived from chitosan and 2-hydroxibenzaldehide and its Fe(II) and Cu(II) complexes were synthesized. The formation Schiff base and complexes were confirmed by spectral studies of

UV Vis, FT-IR and XRD X-ray diffractometer studies showed the presence chitosan characteristic peak in all complexes. The formation complexes of chitosan Schiff base result in the decreased of cristallinity of chitosan. Chitosan Schiff base complexes exhibit antibacterial activity higher than chitosan and chitosan Schiff base.

References

[1] Prakash A, Singh BK, Bhojak N and Adhikari D 2010 Spectrochim. *Acta Part A* 76.
[2] Anthony R, David S T, Saravanan K, Karuppasamy K and Balakumar S 2013 *Spectrochim. Acta Part A* 103.
[3] Brunel F, Gueddari NEE and Moerschbacher B M 2013 *Carbohydr. Polym.* 92.
[4] Guo LDS and Yang J 2012 *Adv. Chem. Eng. Sci. 2*.
[5] Auta M and Hameed BH 2014, *Chem. Eng. J*. 273.
[6] Jin X, Wang J and Bai J 2009, *Carbohydr. Res*. 344.
[7] Dai B, Cao M, Fang G, Liu B, Dong Xv, Pan M and Wang, S 2012 *J Hazard. Mater* 219-220.
[8] Santos JED, Dockal ER, and Cavalheiro ETG, 2005 *Carbohydr. Polym.* 60.
[9] Li Y, Liu C, Tan Y, Xu K, Lu C and Wang P 2014 *Carbohydr.Polym* 110.
[10] Rajavel R, Vavidu MS and Anitha C 2008 *E.J.Chem. 5*.
[11] Eldin MSM, Hasem AI, Omer AM and Tamer TM 2015 *Int. J. Adv. Res* 3.
[12] Miessler GL and Donald AT 1991 *Inorganic Chemistry* Prentice Hall New Jersey.
[13] Hebeish A, Sharaf S and Farouk A 2013 *Int. J. Biol. Macromol*. 60.
[14] Boamah PO, Huang Y, Hua M, Zhang Q, Liu Y, Onumah J, Wang W and Song Y 2015 *Carbohydr. Polym.* 122.
[15] Fatoni A, Kusnarpadi S and Hidayati N, 2010 *Indo.J.Chem* 10
[16] Mangamamba T, Ganorkar MC and Swarnabala G 2014 *Int. J. Inorg Chem. 736538*
[17] Adewuyi S, Kareem KT, Atayese AO, Amolegbe SA and Akinremi CA 2011 *Int. J. Biol.Macromol*, 48

Acknowledgements

We gratefully acknowledge the financial support from DIPA Sriwijaya University. We also thank to Astri Nurmayansih, undergraduate student of Chemistry Department, Faculty of Mathematics and Natural Sciences Sriwijaya University for her valuable help in the part of this research.

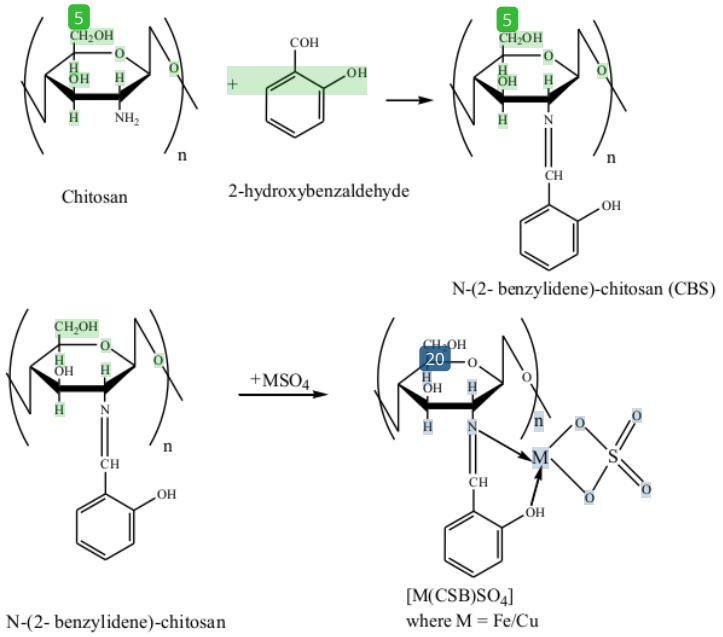

Figure 1. The schematic illustration formation of N-(2-benzylidene)chitosan and its complexes.

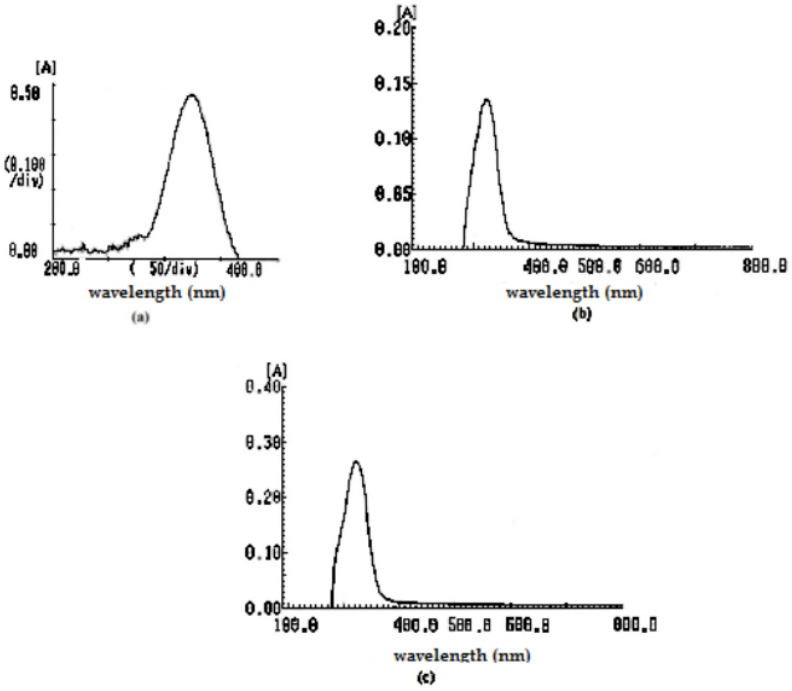

Figure 2. UV-Vis spectrum of CSB (a), CSB-Fe(II) (b) and CSB-Cu(II)(c)

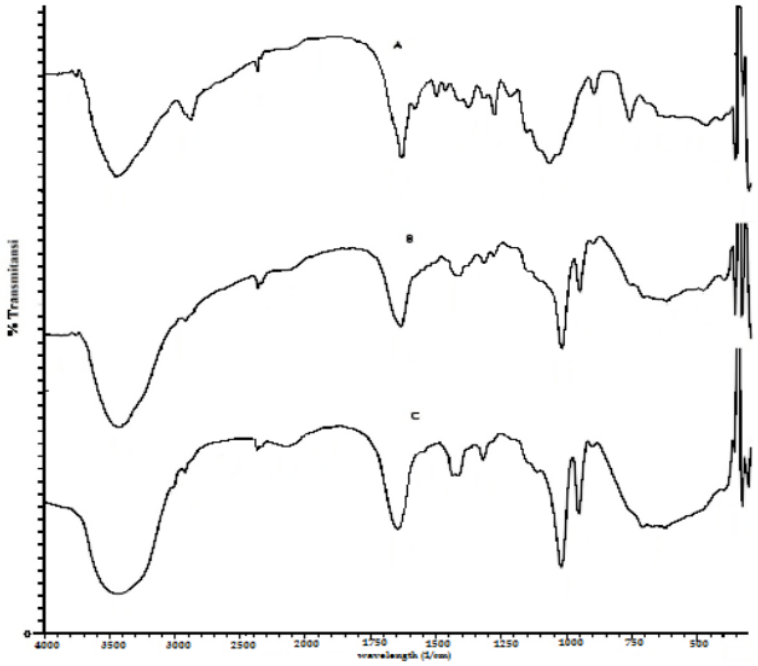

Figure 3. FT-IR Spectrum of CSB (a) CSB-Fe(II) (b) and CSB-Cu(II) (c)

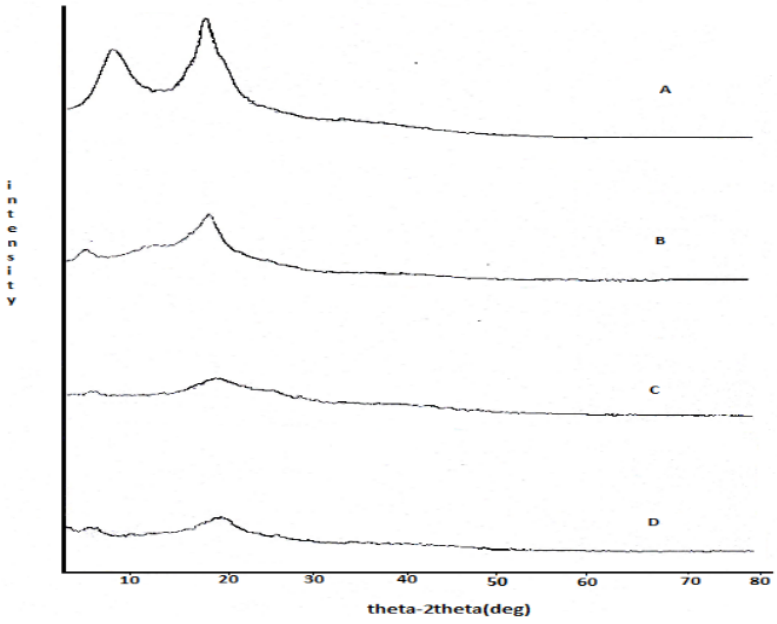

Figure 4. XRD pattern of chitosan (A), CSB (B), CSB-Cu(II) (C) and CSB-Fe(II) (D).

Synthesis and characterization schiff base

ORIGINALITY REPORT

15%	10%	10%	3%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Patel, Mohan N., Anshul P. Patidar, Parag S. Karia, and Pankaj A. Vekariya. "Cytotoxic, antibacterial and nucleic acid interaction studies of square planar palladium(II) complexes", Inorganica Chimica Acta, 2014. Publication	1%
2	www.semanticscholar.org Internet Source	1%
3	www.scilit.net Internet Source	1%
4	jes.ecsdl.org Internet Source	1%
5	Submitted to Canakkale Onsekiz Mart University Student Paper	1%
6	Mustafa Sahin, Hatice Korkmaz, Nuriye Kocak, Ozlem Sahin, Serdar Karakurt, Mustafa Yilmaz. "Synthesis of asymmetrical tridendate Schiff bases and metal complexes and investigation of anticarcinogen effects on	1%

human colon and cervical cancers", Journal of Macromolecular Science, Part A, 2017
Publication

7	www.bartleby.com Internet Source	1 %
8	Hossein Naeimi. "Facile and efficient method for preparation of schiff bases catalyzed by P2O5/SiO2 under free solvent conditions", Heteroatom Chemistry, 01/2008 Publication	1 %
9	Al Dina N. Khoerunisa, Prihati Sih Nugraheni, Mohammad Fahrurrozi, Wiratni Budhijanto. "Selection of Polyanions as Complexation Agent in the Formation of Nanochitosan by Polyelectrolyte Complex Method", Materials Science Forum, 2019 Publication	1 %
10	E. R. Kenawy, F. I. Abdel-Hay, T. M. Tamer, E. M. Abo-Elghit Ibrahim, M. S. Mohy Eldin. "Antimicrobial activity of novel modified aminated chitosan with aromatic esters", Polymer Bulletin, 2019 Publication	<1 %
11	Erdal Canpolat, Mehmet Kaya, Ayşegül Yazıcı. " Mononuclear Chelates Derived from Substituted Schiff Base Ligands: Synthesis and Characterization of a New 3 - Methoxysalicyliden -	<1 %

- Aminoacetophenoneoxime and its Complexes with Co(II), Ni(II), Cu(II), and Zn(II) ", Spectroscopy Letters, 2005
Publication

12	iwaponline.com Internet Source	<1 %
13	Submitted to Universiti Teknologi Malaysia Student Paper	<1 %
14	daneshyari.com Internet Source	<1 %
15	jjees.hu.edu.jo Internet Source	<1 %
16	journal.itera.ac.id Internet Source	<1 %
17	pubs.rsc.org Internet Source	<1 %
18	studentsrepo.um.edu.my Internet Source	<1 %
19	bjbas.springeropen.com Internet Source	<1 %
20	digitalcommons.njit.edu Internet Source	<1 %
21	repository.yu.edu.jo Internet Source	<1 %

22	scitepress.org Internet Source	<1 %
23	upcommons.upc.edu Internet Source	<1 %
24	www.ejurnal.mipa.unsri.ac.id Internet Source	<1 %
25	dspace.nm-aist.ac.tz Internet Source	<1 %
26	Hasanain A. Abdullmajed, H. A. Sultan, Rafid H. Al-Asadi, Qusay Hassan, Asaad A. Ali, C. A. Emshary. "Synthesis, DFT calculations and optical nonlinear properties of two derived Schiff base compounds from ethyl-4-amino benzoate", Physica Scripta, 2021 Publication	<1 %
27	Xinde Zhu, Chenggang Wang, Wen Dong, Fahui Song, Zongqiu Hu, Yuanlin Dang, Hongmei Li, Zhaojie Liu. " SYNTHESIS, STRUCTURE, AND BIOLOGICAL ACTIVITIES OF THE , '-DIETHYLPHOSPHOROHYDRAZONOTHIONATE LIGAND AND COMPLEXES WITH NICKEL(II), COPPER(II), AND ZINC(II) ", Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 2002 Publication	<1 %

28	faculty.uobasrah.edu.iq Internet Source	<1%
29	ijpbs.com Internet Source	<1%
30	R. Menaka, S. Subhashini. "Chitosan Schiff base as eco-friendly inhibitor for mild steel corrosion in 1M HCl", Journal of Adhesion Science and Technology, 2016 Publication	<1%

Exclude quotes	Off	Exclude matches	Off
Exclude bibliography	On		