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Synthesis, Spectroscopy, and Biological Activity of Uranium (IV) Complex with 8-Hydroxyquinoline and Guanidine

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Abstract

A mixed ligand complex of uranium (IV) synthesized from 8-hydroxyquinoline (8-HQ) and guanidine (G) was prepared and studied using infrared spectroscopy (FT-IR) and electronic spectroscopy (UV-VIS). The complex was formed by reacting an equimolar proportion of uranium acetate with 8-HQ and guanidine. The complex's FT-IR data show that the complex is formed via deprotonation of the hydroxyl group of the HQ ligand. Similarly, a positive shift in the vibrational mode of mixed ligand complexes at around 3650 cm^{-1} confirms their coordination via nitrogen donor's HQ and G. The electronic spectrum of uranium complex showed absorption at around 350 nm due to charge transfer transition, which is responsible for the complex's intense orange colour, and it is obvious proof of metal ion coordination with nitrogen and oxygen atoms on the two ligands. Using the well diffusion technique, the produced complex was tested using four strains of various bacteria (*Staphylococcus aureus, Escherichia coli, Klebsiella spp.*, and *pseudomonas spp*.). The complex was more effective against Gram-positive bacteria *S. aureus* and Gram-negative bacteria *Klebsiella spp*.

Keywords: Uranium, 8-hydroxyquinolne, Guanidine, Spectroscopic investigation.

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Introduction

With chemical characteristics that fall between those of transition metals and lanthanides, the actinide elements occupy a unique position in the periodic table *(1, 2)*. The bonding of lanthanides and actinides has also been a topic of discussion over the past 40 years *(3, 4)*. The Urinal (VI) cation, whose chemistry is among the most thoroughly explored for mineralogy (5), is the most characteristic of these ions. It was discovered in 1789 by German scientist Martin Heinrich Klaproth *(6, 7)*. Additionally, there are various varieties of uranium ores in the crust of the earth *(8, 9)*.

The coordination chemistry of uranium has been widely researched since 1800. However, the notion that uranium and a covalent bonding are feasible was only made in the last 15 years attributed to stable, straightforward beginning materials like *(10)*. Additionally, back donation of nitrogen with U (III) has been hypothesized in a number of published complexes *(11, 12)*. While transition metal complexes have received a great deal of attention due to their several natural applications, such as being tumor-hostile, antibacterial, and antiviral *(13)*. The biological activity of uranyl complexes as antibacterial agents has also been shown, and this has generated considerable interest *(14, 15)*.

Finding antibacterial compounds with novel mechanisms of action has always been an important and difficult task *(17)*. It is generally recognized that resistance to the majority of antibacterial medications poses a serious health danger. Since neutral guanidine is one of the strongest donor molecules *(19),* the coordination chemistry of this molecule has significantly increased over the previous 15 years *(18)*. As a result, it has been highlighted in other related studies *(20)*. Numerous natural compounds, either in cyclic form or as terminal groups of pendent substituents, exhibit guanidine functions *(21)*. Despite the biological significance of guanidine derivatives, many methods have lately been employed to produce these substances *(22, 23)*.

A lot of interest has also been shown in complexes of various metals that include 8-hydroxyquinoline "HQ" or its derivatives because of their biological activities and possible use in organic light-emitting diode optical sensors *(24).* It is also an important molecule that, following deprotonation of the hydroxyl group, can coordinate with a variety of metals as a bidentate through the nitrogen atom of the quinolone ring and the oxygen atom *(25)*. Particularly, promising anti-cancer drugs are designed with success using derivatives of 8-hydroxyquinoline *(26).* The supramolecular coordination molecules based on 8-hydroxyquinoline and their derivatives have received particular attention in recent years *(24).* However, the examined ligand's biological and therapeutic potential as an antiseptic, bacteriostat, and fungistatic agent has also been explored *(28).*

The current paper aimed to prepare and characterize the mixed ligand complex of Uranium (IV) with 8-hydroxyquinoline and guanidine ligands and investigate its structure and stoichiometry by IR and UV-VIS spectroscopic methods. Its antibacterial activity has also been investigated.

Materials and Methods

Reagents and solvents

All reagents and chemicals were of analytical grade and utilized as received without any additional purification. 8-hydroxyquinoline (C_9H_7NO, ≥ 99.0) was supplied from Sigma-Aldrich. The uranium (IV) acetate [$UO_2(CH_3COO)_2$] > 99.8) was supplied from Merck, and guanidine was obtained from Kingchem. Ethanol (99.9%) and methanol (99%) were from Merck. Double distilled water was used for all the experiments.

Preparation of metal complex

The complex was synthesized by the method described in the literature *(28)*. A solvent of ethanol, methanol, and double distilled water were used to prepare the two ligands and metal ion solutions, respectively. 2.35 mmol of Uranium (IV) acetate in 10 ml methanol was add slowly to an equimolar quantity of 8- hydroxylquinoline (2.35 mmol) in 10 ml of methanol The mixture was stirred for half an hour at room temperature in an open flask. The temperature was then gradually increased and the reaction mixture was reflux for 5 minutes, till the color of the solution was turned to Orange. After that, 2.35 mmol in 10 ml aqueous solution of guanidine was added to the mixture. The reaction was then refluxed for two hours in water bate till the color was changed to dark Orange. Then, the solution was filtered through Whatman filter paper No. 1 and the precipitate was washed with ethanol first then acetone and finally dried in a vacuum desiccator over anhydrous $CaCl_2$ (Figure 1).

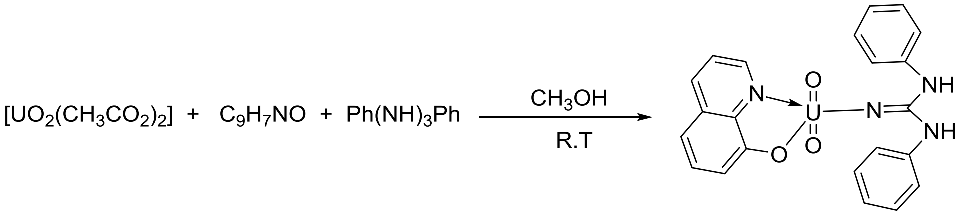

Figure 1. Preparation of metal complex

Spectral analysis

The UV – Visible absorption spectra of 8-HQ, G, and the complex in their solutions were measured over the range of 200–800 nm by Cary 60 spectrophotometer from Agilent Technologies Company. The Fourier transform–Infrared Spectroscopy (FTIR) of 8-HQ, G, and synthesized Uranium complex were carried out over the range of 400-4000 cm^{-1} using Perkin Elmer FT-IR Spectrometer with resolution of 1 cm^{-1}. All measured Spectra were recorded at 25°

Source of Microbial Cultures

Cultures were obtained from department of Microbiology at Moafa Laboratory, Misurata Libya. They include: Four strains of different bacteria (*Staphylococcus aureus, Escherichia coli, Klebsiella spp., and pseudomonas spp.*). The bacterial cultures were maintained in their respective agar at about 5°C throughout the course of the study and used as stock cultures.

In Vitro Antibacterial Activity Testing

Using the well diffusion technique, it was determined whether the uranium complex, 8-hydroxyqunolin, and guanidine had any *in vitro* antimicrobial effects on four different bacterial strains (*Staphylococcus aureus, Escherichia coli, Klebsiella spp.*, and *pseudomonas spp*.). The procedure was carried out in accordance with the suggested standard procedure by Thitilertdecha et al. *(29).* It was done using a 0.5 McFarland standard microorganism cell solution. The Uranium complex, 8-HQ, and G were dissolved in 10 ml of methanol to provide four concentrations for the tested compounds: 0.5, 1, 2, and 5 mg/ml. These concentrations were used for the assay. Approximately 20 µl of each solution from the spread plate culture of each microbial isolate served as the sample volumes applied to the agar wells (The plates were carried out in triplicates). Then, all of the plates containing the examined organisms were given an overnight incubation period at 37°C. Each solution's zone of inhibition for all isolates was noted after 18–24 hours of incubation. The inhibitions zone's diameters were expressed in millimeters (mm). As a control, 5 mg/ml of the common antibiotic ciprofloxacin was utilized.

Results and Discussion:

Electronic spectra of the compounds

The electronic spectra reveal details about the ligand's and its metal complex's electronic structure. Table 1 and Figure 2 contain a list of all compounds' electronic spectra (two Ligands and complexes together). Different bands in the ranges of 200–250 nm and 300–400 nm could be seen in the electronic spectra of all the ligands and metal complexes. The guanidine ligand (G) spectra in ethanol exhibit two highly intense bands with wavelengths of 210 nm and 241 nm, which are attributed to (π→π*) and (n→π*) transitions, respectively. Similar to this, the 8-hyroxyquinoline ligand's (8-HQ) spectrum in the same solvent exhibits signals: two were sharp and appeared at 205 and 242 nm, and the other is broad at 310–315 nm, which are attributed to the (π→π*) and (n→π*), respectively. The complex's UV-Vis spectrum showed three absorption peaks: at 207 nm for (π→π*) in the ligand field, at 250 nm for (n→π*) which is shifted by 8 nm due to the donation of lone pair electrons from nitrogen and oxygen atoms to the metal ions, and the last too broad peak at (350-380 nm) due to Charge Transfer transition, which is responsible for the complex's deep orange colour and is clear evidence of the metal ion coordination with nitrogen and oxygen atoms on the two ligands.

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Table 1. UV-VIS spectral data of guanidine, 8-hydroxyquinoline, and uranium complex

Compound	8-Hydroxyquinoline	Guanidine	Uranium-Complex
λ_{max} (nm)	205	210	207
	242	241	250
	310-315	-	350-380

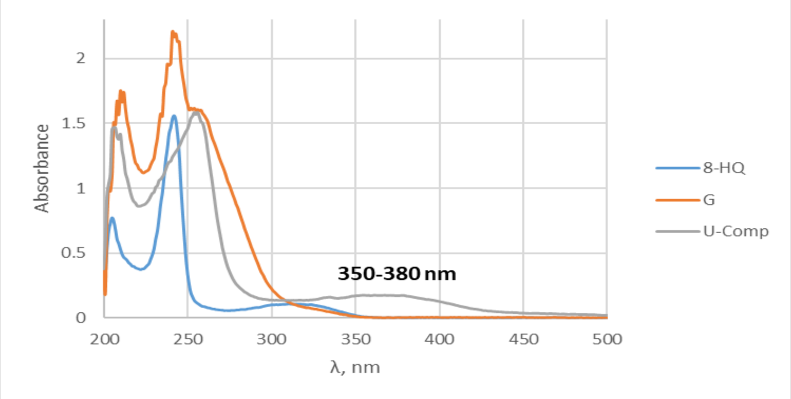

Figure 2. UV-VIS Spectra of guanidine, 8-hydroxyquinoline, and uranium complex

FT-IR spectra of the compounds

The most significant infrared spectral bands that provide conclusive structural evidence for ligand coordination to core metal ions. Table 2 and Figure 3 show the characteristic vibrations and assignments of the ligands (8-QH) and (G) and their complex with uranium(IV). The infrared spectrum of the free ligand (8-HQ) revealed a broad band about (3650) cm-1, which corresponds to the stretching vibrations of v(N-H) + v(O-H), as well as another broad absorption band at (3050) cm^{-1}, which might be explained as v(C-H) stretching. The v(C-H) bending was observed at (1910) cm^{-1}, while the v(C-N) stretching band was observed at 1200 cm^{-1}. A strong v(N-H) stretching band was observed at 3340 cm^{-1} for guanidine ligand. The v(C=C) stretching and v(N-H) bending modes were observed at 1634 cm-1, and a weak band due to v(C-H) bending was observed at 2050 cm^{-1}. The absence of the band between (3000-3500 cm^{-1}) due to the O-H and N-H stretching vibrations of the OH and NH groups of HQ and G, respectively, is a significant characteristic of the infra-red spectra of uranium complexes. This finding supports the theory that the hydroxyl group of the HQ moiety is deprotonated during the complex formation process. Additionally, a positive shift in the vibrational mode of mixed ligand complexes from 3650 cm^{-1} to 3680 cm^{-1} confirms their coordination through the nitrogen donors of HQ and G. Some new weakly bright bands that have been seen in the (650 - 900 cm^{-1}) range may be attributed to M-N and M-O vibrations, respectively. It should be observed that the spectra of the ligands do not contain these vibrational bands.

Table 2. FT-IR spectral data of guanidine, 8-hydroxyquinoline, and uranium complex

Compounds	Observed Frequencies (cm^{-1})				
	O-H, N-H stretching	C-H stretching	C-H, O-H, N-H bending	C-N, C-O stretching	M-N, M-O vibrations
8-Hydroxyquinoline	3650	3050	1910	1200	-
Guanidine	3340	-	2045, 1634	-	-
Uranium-Complex	310-315	-	1380	1100	650-900

Figure 3. FT-IR spectra of guanidine, 8-hydroxyquinoline, and uranium complex

Antimicrobial investigations

The potency of the metal complexes was evaluated against four bacteria. The diameter of the zone inhibitor (mm) was used to compare the antimicrobial activity of the test compounds as shown in Table 3 and Figure 4. The results revealed a variable sensitivity of compound towards the micro-organisms as shown in Table 3. The data showed that all tested compounds have an appropriate activity against all the tested micro-organisms. The complex of Uranium (conc. 5 mg/mL) presented the highest activity against S. *aureus* as Gram-positive bacteria and *Klebsiella sp*p. as Gram-negative bacteria, while the uranium complex with four concentrations showed lower inhibition zones against *Pseudomonas spp.* (Figure 4). In sum, a comparison of the activities among concentrations of complex of Uranium complex, 8-hydroxy, and guanidine indicates a stronger activity with most Gram-positive. In additional, Statistical analysis the results which used ANOVA ONE WAY showed there were significant differences except pseudomonas.

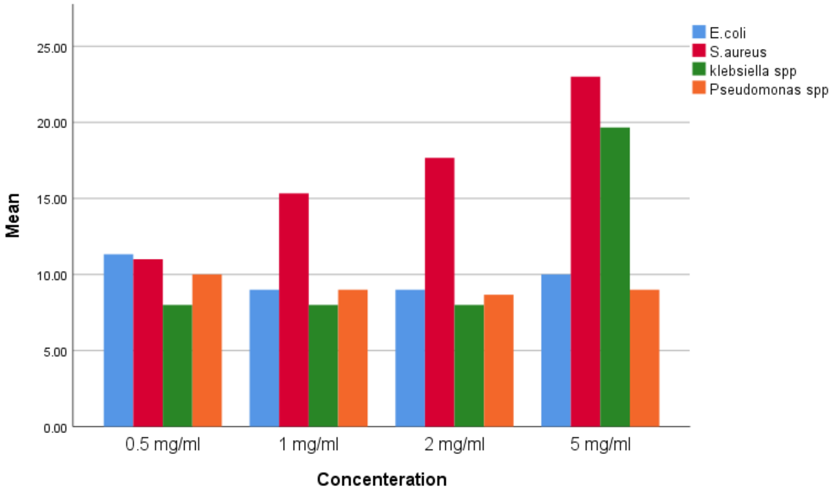

Figure 4. Graph of finding in relation to effective the Uranium complex, 8-hydroxyqunolin, guanidine on Bacteria

Table 3. Analysis of variance (ANOVA) table for antibacterial activity

		Sum of Squares	df	Mean Square	F	Sig.
E.coli	Between Groups	11.00	3	3.67	44.0	0.00
	Within Groups	0.67	8	.08		
	Total	11.67	11			
S. aureus	Between Groups	224.92	3	74.97	179.93	0.00
	Within Groups	3.33	8	0.42		
	Total	228.25	11			
klebsiella spp.	Between Groups	306.25	3	102.08	175.00	0.00
	Within Groups	4.67	8	0.58		
	Total	310.92	11			
Pseudomonas spp.	Between Groups	3.00	3	1.00	3.00	0.1
	Within Groups	2.67	8	0.33		
	Total	5.67	11			

Conclusion

The 8-hydroxyquinoline and guanidine ligands in the mixed ligand complex of uranium were described. Equimolar amounts of the starting materials were reacted to create the complex. The compound was identified using FT-IR and UV-VIS spectroscopic methods. The complex's UV-VIS spectra revealed a new broad band at 350–380 nm as a result of a charge transfer transition. The FT-IR spectra showed that the vibration modes of guanidine and 8-hydroxyquinoline, respectively, vanished at 3340 cm^{-1} and shifted positively to 3650 cm^{-1}. The uranium complex and its two ligands had greater action against the majority of Gram-positive bacteria.

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تحضير، و دراسة طيف، و الفعالية البيولوجية لمعقد اليورانيوم (IV) مع 8-هيدروكسي كوينولين و الجوانيدين

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المستخلص العربي

تم تحضير معقد اليورانيوم (IV) مع 8-هيدروكسي كوينولين (8-HQ) و الجوانيدين (G) و دراسته باستخدام التحليل الطيفي بالأشعة تحت الحمراء (FT-IR) والتحليل الطيفي الإلكتروني (UV-VIS). تم تشكيل المعقد عن طريق تفاعل نسب مولية متساوية من خلات اليورانيوم مع (8-HQ) و الجوانيدين. يُظهر طيف FT-IR الخاص بالمعقد أنه تكون من خلال نزع مجموعة الهيدروكسيل من الليجاند 8-HQ. وبالمثل ، فإن الإزاحة الموجبة في الانتقال الاهتزازي للمعقد المتكون عند حوالي 3650 سم$^{-1}$ يؤكد ارتباطها عبر نيتروجين كل من (8-HQ) و الجوانيدين. أظهر الطيف الإلكتروني لمركب اليورانيوم امتصاصًا عند حوالي 350 نانومتر بسبب انتقال نقل الشحن ، وهو المسؤول عن اللون البرتقالي الداكن للمعقد ، وهو دليل واضح على ارتباط أيون المعدن مع ذرات النيتروجين والأكسجين للمتصلات. باستخدام تقنية الانتشار ، تم اختبار المركب الناتج باستخدام أربع سلالات من البكتيريا المختلفة (*Staphylococcus aureus*، *Escherichia coli*، *Klebsiella spp.*، *pseudomonas spp.*). كان المعقد أكثر فعالية ضد البكتيريا موجبة الجرام *S. aureus* والبكتيريا سالبة الجرام *Klebsiella spp.*.

الكلمات المفتاحية: اليورانيوم، 8-هيدروكسي كوينولين، جوانيدين، دراسة طيفية.