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Abstract

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DNA and HSA Binding Of Copper(II)-Complexes With Imine-Based Ferrocene Derivatives

Gigić, A.[a]*, Caković A. [a], Stevanović, D.[a] , Kesić, A.[b] , Bugarinović, J.[a] , Bogojeski, J.[a]

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Abstract: Copper, a crucial transition metal ion in biological systems, showcases distinctive redox activities and exhibits strong binding affinity toward nucleobases. In this study, three novel copper(II) complexes were synthesized and characterized, employing imine-based ferrocene derivatives as ligands. Characterization was achieved through MS and UV spectrophotometry, followed by an examination of the complexes' reactivity towards biomolecules. Specifically, the interaction of these complexes with CT-DNA and human serum albumin (HSA) were investigated. The findings demonstrate good CT-DNA and HSA interaction ability of the studied complexes.

These results underscore the potential of incorporating imine-based ferrocene derivatives as ligands to enhance the stability and reactivity of copper(II) complexes. This research contributes to expanding the understanding of metal-ligand interactions in biological systems and offers insights into the design of novel metal-based therapeutics.

Acknowledgment

The authors gratefully acknowledge the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, grants numbers. 451-03-66/2024-03/ 200122, 451-03-66/2024-03/200378.

DNA and HSA Binding Of Copper(II)-Complexes With Imine-Based Ferrocene Derivatives

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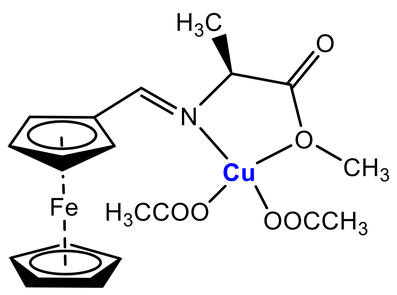
Copper, a crucial transition metal ion in biological systems, showcases distinctive redox activities and exhibits strong binding affinity toward nucleobases. In this study, three novel copper(II) complexes were synthesized and characterized, employing imine-based ferrocene derivatives as ligands. Characterization was achieved through MS and UV spectrophotometry, followed by an examination of the complexes' reactivity towards biomolecules. Specifically, the interaction of these complexes with CT-DNA and human serum albumin (HSA) were performed using UV-VIS spectrophotometry and fluorescence spectroscopy.

COMPLEX 1



*The **mass spectrum** of complex 1 was recorded in positive ion mode. The signal at m/z 480.05 corresponds to the [Cu + L]⁺ adduct.*

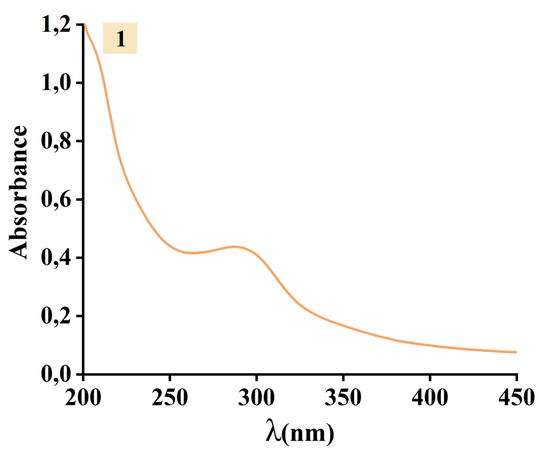


***Fig. 1.** UV spectrum of Complex 1.*

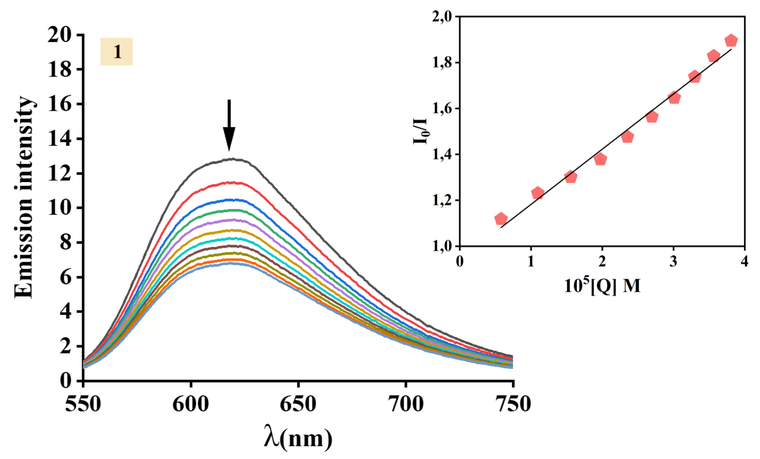


***Fig. 2.** Emission spectra of EB bound to DNA in the presence of complex 1. [EB] = 12,3 μM, [DNA] = 12,3 μM; [complex] = 0-38,1 μM; λex = 527 nm. The arrow shows the changes in intensity upon increasing the concentration of complex. Insert: Stern-Volmer quenching plot of EB/CT-DNA for complex 1.*

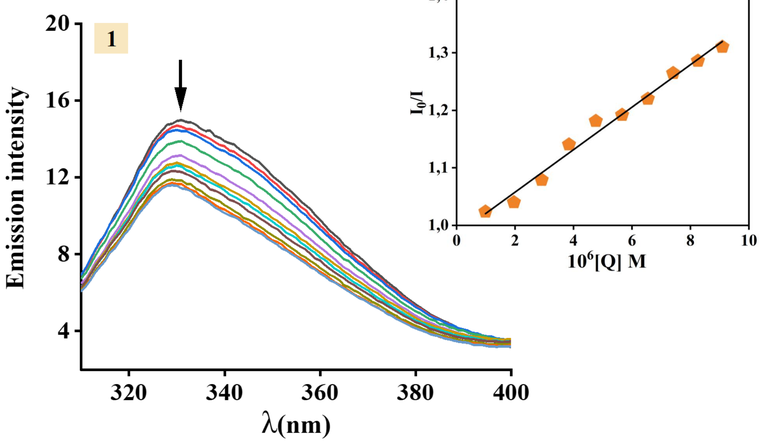
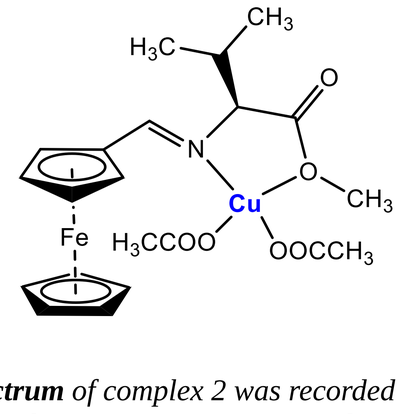


***Fig. 3.** Emission spectra of HSA in presence of complex 1. [HSA] = 2 μM, [complex] = 0-9,1 μM; λex = 295 nm. The arrow shows the changes in intensity upon increasing the concentration of complex. Insert: Stern-Volmer quenching plot of HSA for complex 1.*

COMPLEX 2



*The **mass spectrum** of complex 2 was recorded in positive ion mode. The signal at m/z 507.98 corresponds to the [Cu + L]⁺ adduct.*

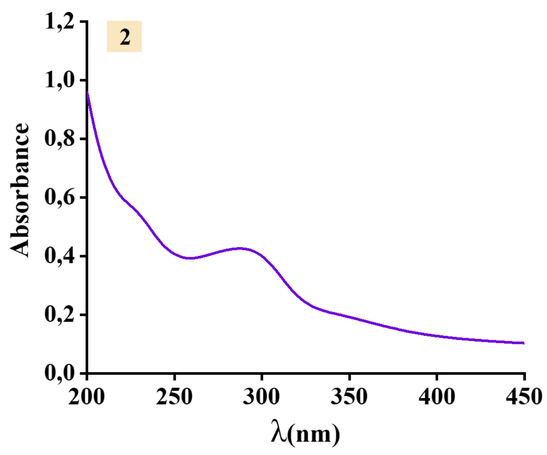


***Fig. 4.** UV spectrum of Complex 2.*

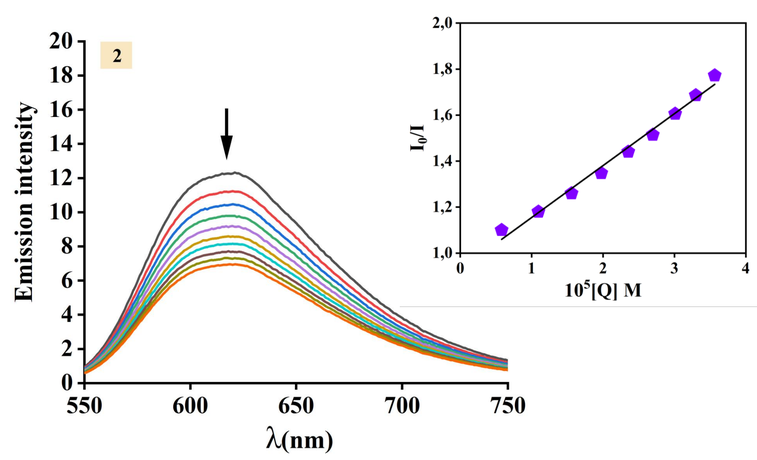


***Fig. 5.** Emission spectra of EB bound to DNA in the presence of complex 2. [EB] = 12,3 μM, [DNA] = 12,3 μM; [complex] = 0-38,1 μM; λex = 527 nm. The arrow shows the changes in intensity upon increasing the concentration of complex. Insert: Stern-Volmer quenching plot of EB/CT-DNA for complex 2.*

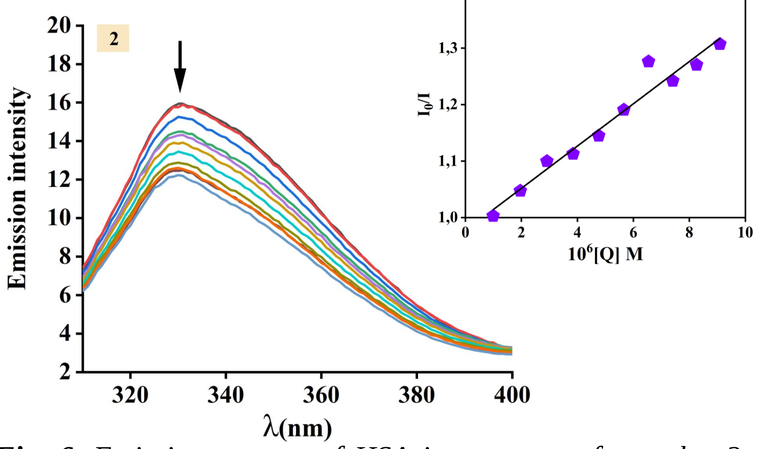
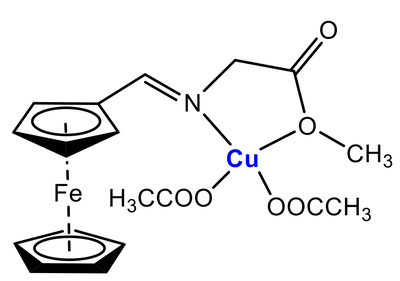


***Fig. 6.** Emission spectra of HSA in presence of complex 2. [HSA] = 2 μM, [complex] = 0-9,1 μM; λex = 295 nm. The arrow shows the changes in intensity upon increasing the concentration of complex. Insert: Stern-Volmer quenching plot of HSA for complex 2.*

COMPLEX 3



*The **mass spectrum** of complex 3 was recorded in positive ion mode. The signal at m/z 465.95 corresponds to the [Cu + L]⁺ adduct.*

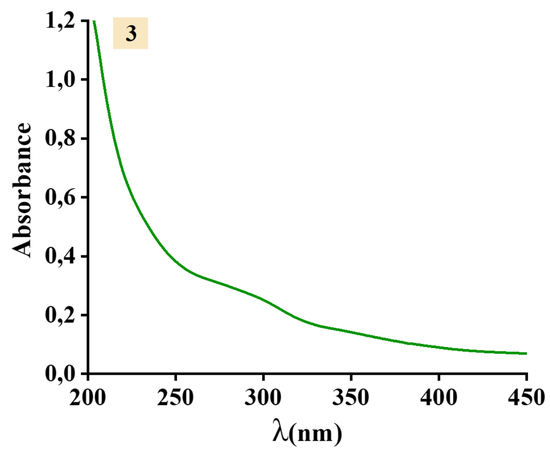


***Fig 7.** UV spectrum of Complex 3.*

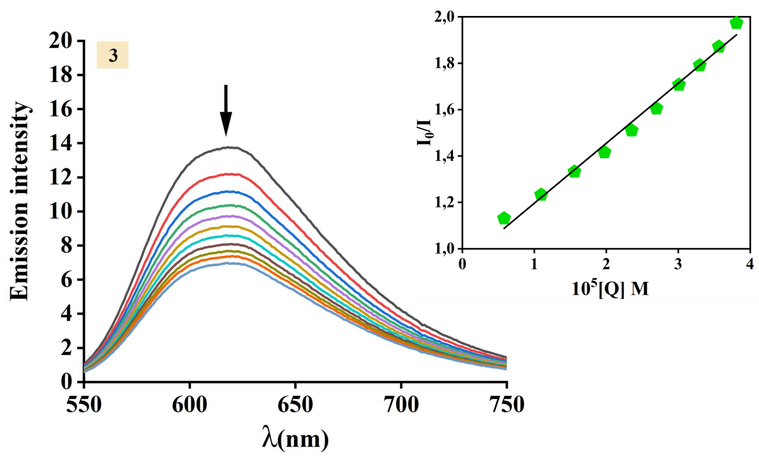


***Fig. 8.** Emission spectra of EB bound to DNA in the presence of complex 3. [EB] = 12,3 μM, [DNA] = 12,3 μM; [complex] = 0-38,1 μM; λex = 527 nm. The arrow shows the changes in intensity upon increasing the concentration of complex. Insert: Stern-Volmer quenching plot of EB/CT-DNA for complex 3.*

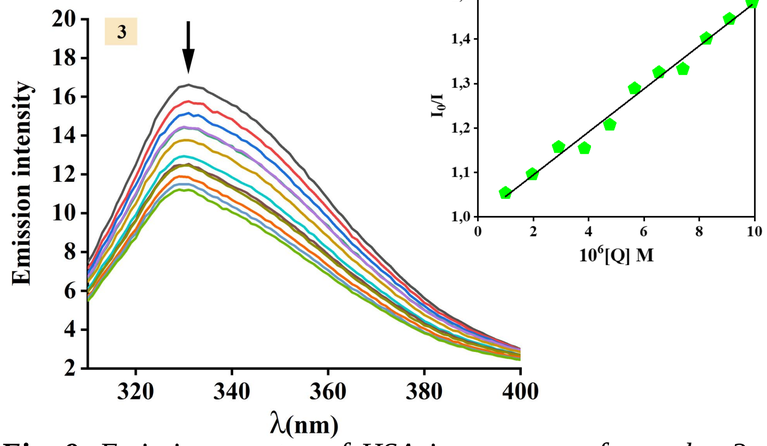


***Fig. 9.** Emission spectra of HSA in presence of complex 3. [HSA] = 2 μM, [complex] = 0-9,1 μM; λex = 295 nm. The arrow shows the changes in intensity upon increasing the concentration of complex. Insert: Stern-Volmer quenching plot of HSA for complex 3.*

	EB/CT-DNK	HSA
Complex	K_{sv} [M^{-1}]	K_{sv} [M^{-1}]
1	$2,4 \times 10^4$	$3,7 \times 10^4$
2	$2,3 \times 10^4$	$3,7 \times 10^4$
3	$2,6 \times 10^4$	$4,8 \times 10^4$

Conclusion:
Based on the obtained spectra, we can conclude that the formation of copper(II) complexes has occurred. The obtained values of binding constants indicate that all three complexes interact moderately with DNA and HSA, with the complexes showing a slightly higher affinity for HSA.

Acknowledgment:
The authors gratefully acknowledge the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, grants numbers. 451-03-66/2024-03/ 200122, 451-03-66/2024-03/200378.