Complexation study of Bi³⁺ metal ion with 8-Hydroxyquinoline based azo dye and its antimicrobial activities

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Abstract

The metal complex between Bi^{3+} and 8hydroxyquinoline-based azo dye (Bi^{3+} -8-HDQ) was prepared and characterized by UV-Visible, IR, SEM and powder XRD analysis. A spectroscopic peak of complex formation appears at 340 nm. The azo dye of 8-hydroxy-quinoline is a typical indicator to determine bismuth ions (III) using the complexometric method. The antimicrobial activity of the complex results in a high zone of inhibition in the range of 12 mm to 14 mm.

Keywords: Bismuth (III), azo dye, UV-visible study. Scanning Electron Microscopy, EDX.

Introduction

Metal complexes have been developed and produced using 8-hydroxyquinoline ligands^{2,10,18,23}. 8-hydroxyquinoline is known as an effective chelator for metal ions and has found significant applications in the study of metal $complexes^{7,15,19,24}$. Due to their lack of rotational symmetry which enhances noncentrosymmetric, quinolines are very desirable materials. Quinoline has two rings: a pyridine ring and a benzene ring which serve respectively as the acceptor and donor group. Due to the enhanced dyeing properties of transition metal complexes of azo compounds, they are receiving significant attention from researchers. Fabrics dyed using metal complexes in nylon fibers have been reported for good light fastness^{1,14}.

Several transition metal complexes with azo ligands have been reported to have a variety of chemical, physical, catalytic, photophysical and photochemical properties^{3,6,9,12,16,22}. After the hydroxyl group has been deprotonated, the 8-hydroxy quinoline molecule can coordinate with different ions as a bidentate ligand through the nitrogen and oxygen atoms of the quinoline ring^{4,13,18}. For their biological significance and ability to coordinate with metal ions, quinoline and its derivatives have chemical characteristics¹⁷. A number of quinoline compounds have chemotherapeutic potential and function as anti-allergic, anti-malaria and anti-malaria medications¹¹.

8-hydroxyquinoline (Fig. 1) is one of the vital derivatives of quinoline and their chelation property for various metal ions also has antibacterial activity^{5,21}. Various 8-hydroxyquinoline transition metal compounds based on azo dyes have been discovered.



Figure 1: 8-Hydroxyquinoline azo dye

Material and Methods

Chemicals and Instruments: All chemical compounds used in this study were supplied by S.D. Fine Chemicals. Electronic spectra were measured with a single beam UV-VIS Bio-Era spectrophotometer with quartz cell (10mm). IR spectrometer of Brucker was used to obtain the FT-IR spectra. Milli-Q provided additional purification of double distilled water. Solvents of the AR grade were employed. The stock solution of 8-HDQ dye was made of 2×10^{-4} M and metal solutions were of 1×10^{-2} M.

Complexation Study: The ligand and bismuth metal ion were dissolved in a 5×10^{-5} M solution. For complexation investigation, metal ions solution was incrementally added to the ligand.

Antimicrobial Activity Study: Utilizing three grampositive bacteria (*S. aureus*) and two gram-negative bacteria (*E. coli* and *Samonella typhi*), the ligand and its complex were examined for their *in vitro* antibacterial properties. Solutions of three different concentrations were prepared i.e. 0.01, 0.5 and 1mg/L prepared by dissolving the complex and 8-HQ in ethanol. 100 μ L of sample was put to each agar well. As a control, ciprofloxacin (conc. 1 mg/mL) was employed.

Results and Discussion

UV-visible study: In an ethanol solution, the complexation of Bi^{3+} (5× 10⁻⁵ M) with 8-HDQ (5× 10⁻⁵ M) was studied. A prominent band at 350 nm is visible in the free ligand's UV-VIS spectra and is caused by the π - π * transition (Fig. 2). The complex structure is revealed by an intensity drop and a minor band-to-wavelength shift. Here, we also experimented with the spectra of the synthesized complex of Bi^{3+} -8-HDQ azo dye in an ethanol solution which exhibits a significant

loss in intensity along with a minor band to the blue shift. This significant drop in complex intensity can be caused by the metal effect which has a substantial affinity for the ligand. It is obvious from these data that Bi³⁺ has a strong affinity for 8-HDQ.

Stoichiometry of the Complex: 8-HDQ azo dye and metal ion Bi^{3+} solutions were combined in the same mole ratios while keeping the dye and metal ion concentration constant. The absorbance was measured at 340 nm wavelength to estimate complex stoichiometry. Figure 3 displays the absorbance graph against mole fractions. The reaction stoichiometry of Bi^{3+} - 8-HDQ 1:2 is indicated by the highest absorption being found for a mole ratio of 0.4. Hence it is confirmed that two ligands are attached to a metal ion.

Effect of pH on complexation: The impact of pH is investigated to compare how complexation is affected. 8-HDQ's pH range was pH 1 to pH 10. For complexation, 350 nm absorbance was measured. The graph shows that complex formation is significantly influenced by pH. The complex is initially more readily absorbed when pH rises (Figure 4), but this is quickly followed by a dramatic increase at pH 3. However, as solution pH rises, absorption significantly decreases and saturation occurs in the pH range of 4 to 8. pH 3 was chosen for research.



Figure 2: UV-Visible spectra of ligand and its complex



Figure 3: Jobs plot of Complex for the stoichiometry

Scanning Electron Microscopy: Figure 5 displays SEM pictures of 8-HDQ to better understand its morphology and how it interacts with metal ions from the Bi³⁺ ion. The particle size of 8-HDQ and complex was in the range of 1 to 2 μ M. SEM analysis distinguishes the complex from the pure ligand. Even though 8-HDQ showed a consistent cell pattern, the complex showed a clear modification in

morphology. The regular cells merged when the complex with Bi^{3+} was formed. Additionally, energy dispersive spectroscopy was used to evaluate figure 6 to see if bismuth was present in the complex (EDS). EDS measurements provide qualitative data regarding the development of the complex between Bi^{3+} and the 8-HDQ azo dye.



Figure 4: Effect of pH on Complexation of Bi³⁺ - 8-HDQ complex.



Figure 5: SEM micrograph of (a) 8-Hydroxyquinoline azo dye and (b) Bi³⁺ - 8-HDQ complex.

 Table 1

 The stability constant of the prepared complex:

 As
 Am
 α
 Log k

0.01515

4.3×105

1.728

2.795

2.383

Complex

 $[Bi(L)_2]$



Figure 6: Energy dispersive spectra of the Bi³⁺ - 8-HDQ complex

Stability constant: Stability constant is the equilibrium constant for complex formation in solution, also known as a binding constant. It is a gauge of the metal and ligands potential for strong binding when they come together to create a complex. With the aid of spectroscopic data, the (1:2) metal: ligand complex's apparent stability constant (K) was derived using the equation:

$K=1-\alpha/4\alpha^2c^2$	(1)
$\alpha = A_m - A_s / A_M$	(2)
Or $\alpha = A_S - A_m / A_s$	

where c is the complex solution's concentration in mol/L, A is the degree of dissociation and A_S is the solution's absorption when ligand and metal ions are present in stoichiometric amounts. Am=is the absorption of a solution with excess ligand and the same amount of metal⁵. The value of A_S and Am was measured at λ_{max} of the solution, the values of Am, AS, α , K were tabulated below table 1 showing the high value of K i.e. 4.3×10^5 . This result shows that Bi³⁺ metal has strong binding with 8-HDQ azo dye.

FTIR analysis and the complex's probable structure: It is feasible to understand the mechanism of interaction between Bi³⁺ and 8-HDQ by studying the FTIR spectra of the ligand and its complex (Fig. 8). A band from the phenolic -OH group of the azo dye, which was initially present at 3339 cm⁻¹ and migrated to 3366 cm⁻¹ in the complex, supported the formation of the complex. The stretching frequency resulting from C-N vibration shifts to 1362 cm⁻¹ in complex dye and falls to 1336 cm⁻¹ in azo dye. The band assigned to -N=N- was at 1558 cm⁻¹ which is shifted to 1532 cm⁻¹. The newly formed band appears at 511 cm⁻¹ in the complex, which may be due to the M-N bond.

The probable structure of the Bi^{3+} complex is shown in fig. 7. The stoichiometry is Bi^{3+} - 8-HDQ 1:2 and the FTIR spectroscopic analysis revealed M-L interaction via the phenolic -OH group. However, crystallographic research is needed to determine the complex's precise structure.



Figure 7: Proposed structure of Bi³⁺ - 8-HDQ complex

Powder XRD-Analysis: Using powder XRD, the 8-HDQ azo dye and its metal complex 8-HDQ-Bi³⁺ were investigated throughout the range of $2\theta = 10-90^{\circ}$. According to the complex's powder XRD patterns, which differ from those of the initial ligand 8-HDQ, coordination compounds have formed where the peak with the highest intensity was located when it was observed at $2\theta = 31.84$ of the ligand. It is now $2\theta = 31.58$ in the complex. Table 2 summarizes the results and is shown in figure 9. The 8-HDQ-Bi³⁺ complexes appear to have limited crystallinity based on the patterns' nature. Using the Scherrer formula, the average particle size of the ligand and metal complexes was determined.

$$D = \frac{K\lambda}{FWHM \times cos\theta}$$

where K = Scherrer constant, FWHM = whole breadth at half the maximum of the diffraction pattern's reflection peak which has the same maximum intensity, λ = wavelength of X-rays (1.54059 Å) and θ = diffraction angle of X-rays. The Scherrer constant (K) in the equation, which takes into account the geometry of the particles, is typically believed to be 0.9. The ligand and its complexes have average particle diameters of 13.40 and 19.88 nm, respectively. Similarly, XRD studies of azo dye complexes based on 5-nitro8-hydroxyquinoline were $mode^{13}$.

Antimicrobial Activity: Table 3 displays the 8-HDQ and Bi^{3+} complexes' antibacterial activities. Pathogenic bacteria such *E. coli, Salmonella typhi* and *S aurious* were used to investigate the antimicrobial activity of the ligand and its complexes at concentrations of 0.01, 0.5 and 1 mg/mL.



Figure 8: IR spectroscopic analysis of 8-HDQ azo dye and its Complex



Figure 9: XRD patterns of 8-HDQ and its complexes

ARD data for 6-11DQ and its 6-11DQ-bit complexes									
20°	d(Å)	FWHM	Intensity	D(nm)	20°	d(Å)	FWHM	Intensity	D(nm)
		Ligand					Complex		
12.44	7.108	0.45	14		11.59	7.624	0.174	35	
14.37	6.158	0.423	65		12.11	7.30	2.02	73	
15.44	5.732	1.018	163		22.33	3.8087	0.27	13.6	
20.1	4.414	1.22	67		25.81	3.450	1.57	161	
32.53	2.7502	0.79	337	13.4					19.88

 Table 2

 XRD data for 8-HDQ and its 8-HDQ-Bi ³⁺complexes

Table 3
Inhibition zones for 8HDQ and Bi ³⁺ -8-HDQ azo dye complexes.
Inhibition zone [mm]

minoteon zone [min]								
	Concentration		Bi ³⁺ -8-HDQ					
Bacteria	(mg/L)	8-HDQ Azo Dye	Azo Dye					
	0.01	10mm	12mm					
	0.5	14mm	12mm					
E. Coli	1	10mm	-					
	0.01	11mm	14mm					
	0.5	12mm	-					
S. aurius	1	12mm	14mm					
	0.01	-	-					
	0.5	12mm	_					
Salmonella typhi	1	11mm	12mm					

The results were based on the mean of three replicates. Against all pathogenic bacteria, complex exhibits a lot of microbiological activity. The findings demonstrated that the complex has a sizable inhibitory zone compared to the ligand. *S. aurius* exhibits effective suppression over a 14 mm zone at both low and high concentrations.

Conclusion

In conclusion, we have successfully synthesized a complex of 8-hydroxyquinoline with bismuth (III). Bi³⁺ binding with 8-HDQ has been investigated using UV-Vis spectroscopy. The stoichiometry of both metal ions and ligands has been investigated and established as 1:2. Also the effect of pH on complexation has been studied. The stability constant of the complex formed between bismuth and azo dye of 8-hydroxy quinoline is higher, so the complex formed is stable.

Further, IR spectra, XRD and SEM studies demonstrate binding interaction between Bi^{3+} and ligand. There is significant antimicrobial activity against pathogenic bacteria in this complex.

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References

1. Ali N. F., Saadia A. and Abd El-Megied, Synthesis of new metal complex dye and its application on nylon fibers pretreated with chitosan, *International Journal of Agricultural Technology*, **17**(2), 399 (**2021**)

2. Chen B., Xu L., Liu X., Zhou H., Xu H., Fang X. and Wang Y., Mixed ligands 8-hydroxyquinoline aluminum complex with high electron mobility for organic light-emitting diodes,*Applied Physics Letters*, **92**, 103305 (**2008**)

3. Carlucci L., Ciaxi G., Proserpio D.M. and Rizzato S., Silver(i) polymeric coordination frameworks assembled with the new multimodal ligand 2,2'-azobispyrazine, *New J. Chem.*, **27**, 483–489 (**2003**)

4. Dixit B. and Patel J.A., Spectrophotometric Determination of Paracetamol drug using 8-hydroxyquinoline, *International Journal of Pharmaceutical Sciences and Research*, **5**(6), 2393-2397 (**2014**)

5. Deb B.K. and Ghosh A.K., Chelated compounds and derivative of β -alkoxycarbonylalkyltin chlorides-5-arylazo-8-quinolinolates, alizarinates and thiocyanate: preparation and spectroscopic studies, *Can. J. Chem.*, **65**, 1241–1246 (**1987**)

6. Haytham Elzien A.A., Ahmet A., Selçuk A. and Zafer O., Highly efficient dye-sensitized solar cells based on metal-free and Copper(II) phthalocyanine bearing 2-phenylphenoxy moiety, *Dyes Pigm.*, **124**, 180-187 (**2016**)

7. Jiang P. and Guo Z., Fluorescent detection of zinc in biological systems: recent development on the design of chemosensors and biosensors, *Coord. Chem. Rev.*, **248**, 205-229 (**2004**)

8. Jarad A.J., Synthesis and Characterization of New Azo Dye Complexes with Selected Metal Ions, *Journal of Al-Nahrain University*, **15(4)**, 74-81 (**2012**)

9. Joseph K.L.V., Anthonysamy A., Easwaramoorthi R., Shinde D.V., Ganapathy V., Karthikeyan S., Lee J., Park T., Rhee S.W.,

Kim K.S. and Kim J.K., Cyanoacetic acid tethered thiophene for well-matched LUMO level in Ru(II)-terpyridine dye-sensitized solar cells, *Dyes Pigm.*, **126**, 270-278 (**2016**)

10. Maayan G., Dayagi Y., Arad-Yellin R., Shimon L.J.W. and Shanzer A., Stabilization of unique valencies of cobalt, nickel and copper by complexation with the tridentate ligand 2-(2' pyridyl)-8-hydroxyquinoline, *Polyhedron*, **64**, 365-370 (**2013**)

11. Mekheimer R., Ahmed E.K. and Khattab A.F., A Novel Nucleophilic Substitution with Quinoline Derivatives. Synthesis of Quinolones and Pyrazolo[4,3-c]quinoline Derivatives, *Bull. Chem. Soc. Jpn.*, **66**, 2936–2940 (**1993**)

12. Neuthe K., Bittner F., Stiemke F., Ziem B., Du J., Zellner M., Wark M., Schubert T. and Haag R., Phosphonic acid anchored ruthenium complexes for ZnO-based dye-sensitized solar cells, *Dyes Pigm.*, **104**, 24-33 (**2014**)

13. Nadia A.El., Wakiel H.F. and Rizk S.A., Ibrahim, Synthesis and characterization of metal complexes of azo dye based on 5-nitro-8-hydroxyquinoline and their applications in dyeing polyester fabrics, *Appl Organometal Chem*, **31**(10), 1-7 (2017)

14. Perkins W.S., Textile Coloration and Finishing, Carolina Academic Press, Durham, NC, 123 (**1996**)

15. Soroka K., Vithanage R.S., Phillips D.A., Walker B. and Dasgupta P.K., Fluorescence properties of metal complexes of 8-hydroxyquinoline-5-sulfonic acid and chromatographic applications, *Anal. Chem.*, **59**, 629-636 (**1987**)

16. Shahenda M., Fatmah A.M. and Hussein I.El., Substituted thiazoles VII. Synthesis and antitumor activity of certain 2-(substituted amino)-4-phenyl-1, 3-thiazole analogs, *Bioorg. Med. Chem. Lett.*, **22**, 6318-6323 (**2012**)

17. Shoair A.F., El-Bindary A.A., El-Sonbati A.Z. and Younes R.M., Novel structural and properties models of uranyl with quinoline azo dyes, *Spectrochim. Acta A*, **57**, 1683–1691 (**2001**)

18. Vashi R.T., Patel S.B. and Kadiya H.K., Synthesis, Characterization and antimicrobial Activity of Metal Chelates of 2-[(8-hydroxyquinolinyl)-5-aminomethyl]-3-(4-Bromophenyl)-3(H)- -quinazolin-4-one, *Der Pharma Chemica*, **4(4)**, 1506-1511 (2012)

19. Valeur B. and Leray I., Design principles of fluorescent molecular sensors for cation recognition, *Coord. Chem. ReV.*, **205**, 3-40 (**2000**)

20. Vashi R.T., Patel S.B. and Kadiya H.K., Synthesis, Characterization and Antimicrobial Activity of Metal Chelates of 2-[(8-hydroxyquinolinyl)-5-aminomethyl]-3-(4-Bromophenyl)-3(H)- quinazolin-4-one, *Der Pharma Chemica*, **4(4)**, 1506-1511 (2012)

21. Wang X., Feng L. and Chen Z., A Synthesis and photophysics of novel 8-hydroxyquinoline aluminum metal dye with hole transfer groups, *Spectrochim. Acta*, **71**, 1433–1437 (**2008**)

22. Zollinger H., Color Chemistry Synthesis, Properties and Applications of Organic Dyes and Pigments, third ed., Wiley-VCH, Zurich (2003)

23. Zborowski K.K., Solá M., Porter J. and Proniewicz L.M., Aromatic properties of 8-hydroxyquinoline and its metal complexes, *Cent. Eur. J. Chem.*, **11**(5), 655-663 (**2013**)

24. Zelder F., Brunner Z. and Kramer J. R., DNA-templated catalysis using a metal-cleavable linker, *Chem. Commun.*, **7**, 902-903 (**2004**).

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