

Synthesis and Spectral studies of some (IIb) ions with 2 – [(6 – Nitro – 2 – Benzothiazolyl) azo – 4 , 5 – diphenyl imidazole and Their Biological Activity

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Abstract

This study is concerned with imidazole azo reagent (6 – NO₂ BTADI) 2 – (6 – nitro – 2 – benzothiazolyl) azo] – 4 , 5 – diphenylimidazole and its complexation with (Zinc(Zn⁺²), Mercury(Hg⁺²)) ions .

The optimum conditions of these complexes were studied , such as pH values , The effect of time and temperature on a formation of the complexes .Beers law is obeyed in the concentration rang of (1-10)ug.ml⁻¹. The expected structures of these complexes were obtained by mole ratio method , the result showed that all of these complexes have amole ratio (1 : 2) (metal : reagent) .

Stability constants calculations and melting points measurements , conductivity , IR , UV – Vis spectra and antibacterial activity of the complexes were done.

Key words 2-[(6-nitro-2-benzothiazolyl) azo -4,5- diphenyl imidazole , Zn(II), Hg(II) spectrophotometer.

-) for this reason a number of these ligands were prepared as chelating reagents In this work , the results presented show that 2 – [(6 – Nitro – 2 – benzothiazolyl) azo)]- 4 , 5 – diphenylimidazole (6 – NO₂ BTADI) , which was prepared by Al – adely (10) , is a sensitive , and selective reagent for the spectrophotometric determination of Zn (II) and Hg (II) .

Introduction :

A great number of azo dyes have involved much care as they are sensitive chromogenic reagents (1) . In adding their to use as reagents for spectrophotometer and extraction photometric determination of transition elements ions (2-5) .

The metal complexes of these compound have many uses in biology and industry (6-8) and in organic synthesis (9) . The ligand is isoelectronic with (a – imine) and the active role is the (p – acidic) azo imine group (- N = N – C = N

sodium hydroxide and 50 ml of 10% sodium carbonate . The prepared diazonium solution followed by addition of was then added drop wise to this solution for coupling at (0 – 5) °C for three hours with stirring . The mixture was allowed to stand overnight , and the solid product was filtered off . The product was recrystallized from ethanol and then dried in an oven at 50 °C for several hours. The yield was 75% of dark crystals .

Preparation of complexes :-

The complexes were obtained , by adding (2 mmol) from the ligand (dissolved in hot ethanol 50ml) drop wise with vigorous stirring to a amount (1 : 2) for Zn (II) and Hg (II) chloride dissolved in 15 ml hot distilled water . The mixture was heated to 50 °C for 30 min until the solid compounds precipitated , the precipitate was filtered , washed with ethanol and dried in a desiccator over anhydrous CaCl_2 .

Result and Discussion :-

Absorption Spectra :

The absorption spectra of reagent (6 – NO_2 BTADI) show absorption maximum at 275 nm , 370 due to the (π - π^*) and 471 nm due to the (n - π^*) from aromatic ring through the azo group (charge transfer), these results agree with earlier work(12) . The ligand and its complexes with Zn (II) and Hg (II) ions

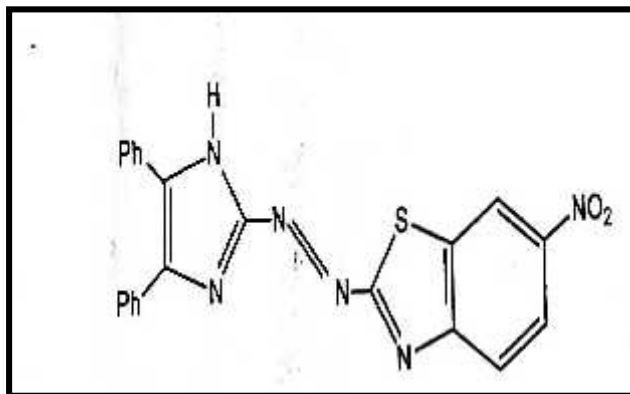


Fig 1: Structure of the reagent (6 – NO_2 BTADI)

Materials & Methods

All chemical used were of high purity (BDH) , Fluka or Aldrich) and used without further purifications except 4 , 5 – diphenyl imidazole which was prepared according to literature(11) .Electronic spectra were recorded on a Shimadzu UV – 1650 double beam spectrophotometer using 1cm quartz cells . IR spectra were recorded with FT– IR– 8400Shimadzu using KBr disc . pH measurements were carried out with a Philips PW 9421 pH meter .

Synthesis and characterization of Azo Reagent (6 – NO_2 BTADI)

A diazonium solution was prepared by taking 1.8 gm (0.01 mol) of 2 – amino – 6 – nitro benzothiazole dissolved in 6 ml of (12) hydrochloric acid then 50 ml of distilled water was added . To this mixture a solution 0.7 gm (0.01 mol) of sodium nitrite in 30 ml of distilled water was add drop wise at (0 – 5) °C . A 2. 2 gm (0.01 mol) from 4 , 5 – diphenyl imidazole was dissolved in 300ml ethanol , then added 50 ml of 10%

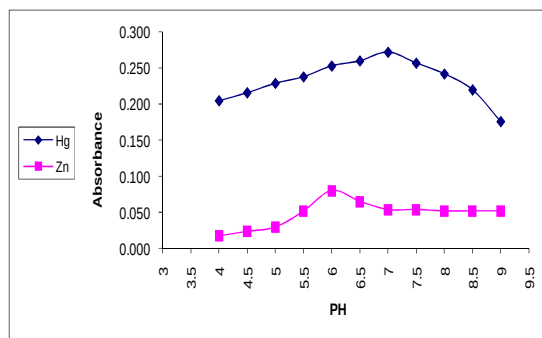


Fig 3: The effect of pH on the absorbance of Zn (II) and Hg (II) complexes

Metal Ratios :

The metal ligand ratios of complexes were resolved by the method of molar ratios the method used to determine the metal in solutions (13). In Fig(4) the results shown the formation of (1:2) (M:L) for complexes at stable wave length of full absorption , these results agree with earlier work (14) .

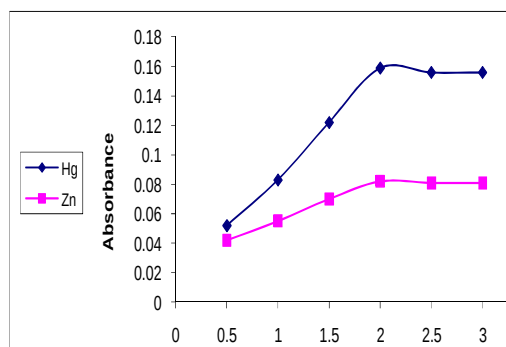


Fig 4: Mole ratio (M:L) of metal chelates Zn (II) and Hg (II) complexes

Infrared spectra :-

Completely the spectra were recorded in the solid state using (KBr) disc in the range (400 – 4000) cm^{-1} . The spectra are convoluted owing to the extensive overlap of a number of bands arising due to $\nu(\text{C-H})$, $\nu(\text{C=N})$, $\nu(\text{N=N})$ in addition other bands originate from

were studied in aqueous ethanolic solution . A bathochromic shift are 525 nm and 537 nm belong to Zn(II) and Hg (II) complexes respectively, the wave length different($\Delta \lambda_{\text{max}}$) is (34-66 nm) . The electronic spectra of the metal complexes of Zn (II) and Hg (II) are given in fig (2) . No d→d transition bands occur in UV-Vis spectra of Zn (II) and Hg(II) complexes

with this ligand . The magnetic susceptibility of the complexes have diamagnetic moments.

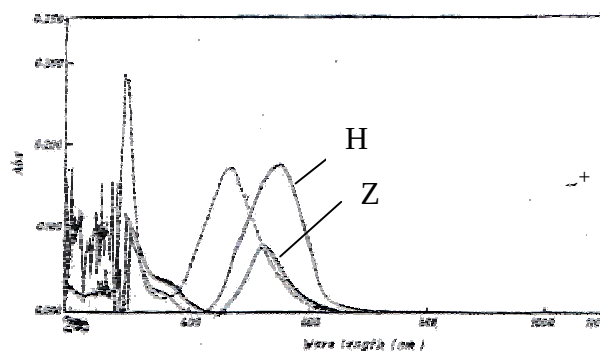


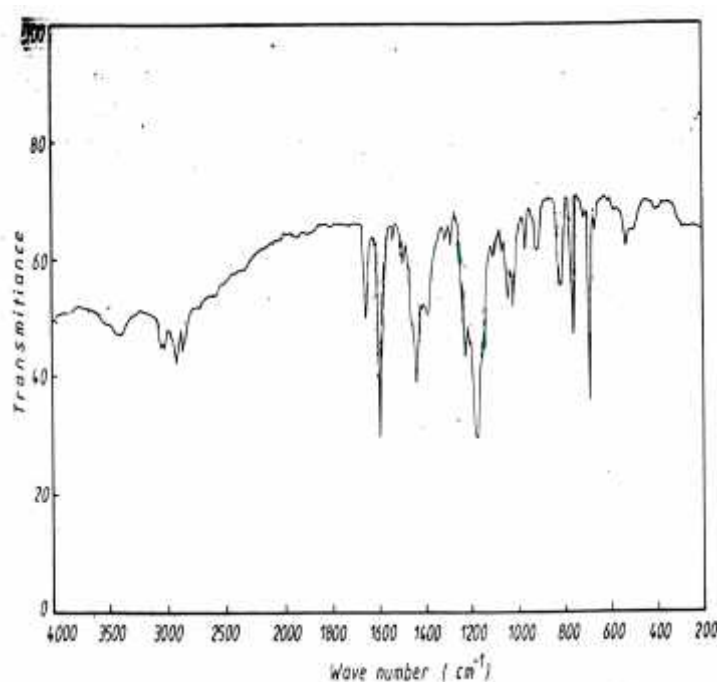
Fig 2: Absorption spectra of reagent (6 – NO₂ BTADI) and (6 – NO₂ BTADI) complexes

Effect of pH :-

Apposite pH values for complex formation were found to be in the range of (4 – 9.5) . For estimate of the optimal pH values for determination of Zn (II) and Hg (II) the effects of pH on the absorbance were studied results are shown in Fig (3)

may indicate that azo group is coordinated to the metal ions (18) .

5. Several other new bands appeared in the (410 – 580) cm^{-1} region these bands did not present in the spectrum of the reagent which the may be attributed $\nu(\text{M-N})$ (21-19). Fig are (5 and 6) show the spectra of reagent (6 – NO_2 BTADI) and



(6 – NO_2 BTADI – $\text{Hg}(\text{II})$ complex

Fig 5: IR spectrum of the ligand (6 – NO_2 BTADI)

imidazole and thiazole rings .The shifts in the position or change in shape of the complexes bands . Linked with these absorption band due to free ligand may suggest a probable modes of bonding in the complexes . Several of these main shifts a long with the conclusions are given below .

1.A novel broad medium band observed at $3393\text{--}3346\text{ cm}^{-1}$ in the spectra of the latter complexes which may indicates the presence of water molecule in them.

2.The weak bands observed at 3120 cm^{-1} and 2910 cm^{-1} in the spectrum of the ligand are due to $\nu(\text{C-H})$ aromatic and aliphatic individually . These bands are stable in position as well as in intensity for both ligand and metal chelates .

3.The spectrum of ligand shows absorption bands at 1580 cm^{-1} and 1595 cm^{-1} due to $\nu(\text{C=N})$ of imidazole and thiazole rings respectively (15) .These bands $\nu(\text{C=N})$ of imidazol ring shifts to lower frequency $1540\text{--}1535\text{ cm}^{-1}$ in the metal complexes, these shifts suggest the linkage of metal ion with nitrogen .

4.Two absorption bands are observed at 1500 cm^{-1} and 1430 in the reagent spectrum which are due to the azo $\nu(\text{N=N})$ (16-17) . The positions of these bands in the spectra of complexes are shifted to a lower frequencies ($1435\text{--}1410$) cm^{-1} with decreased in intensity . Both bands are shifted and reduced intensities this

fixed wavelength . The degree of formation of the complexes (β) is obtained from the relationship (22) . $\beta = (1 - a/a^3 c^2)$ and $a = (A_m - A_s) / A_m$ where A_m and A_s are the absorbance of the partially and full formed complex respectively the optimum conditions the stability follows the sequence $Zn(II) > Hg(II)$ this results agree with the earlier work (23) .The calculated (β) and ($\log \beta$) values are listed in table(1) .

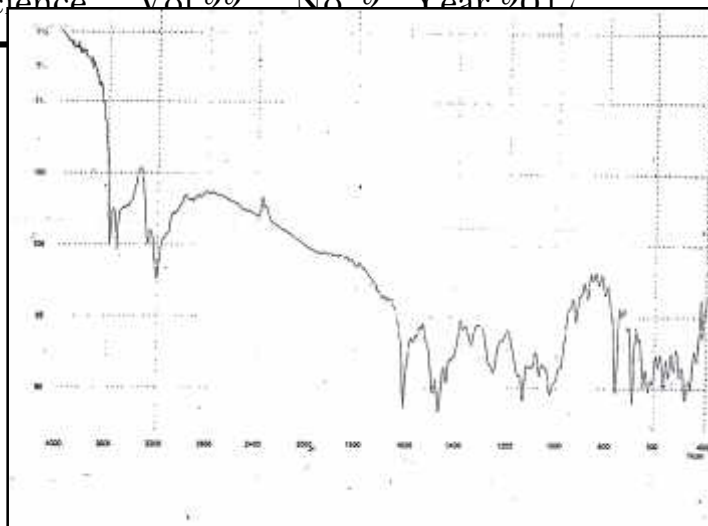
Conductivity Measurement :-

The complexes of $Zn(II)$ and $Hg(II)$ expansion the molar conductivity measurement values $1.44 \text{ S.mol}^{-1}.\text{cm}^2$ and $3.01 \text{ s.mol}^{-1} . \text{cm}^2$ in DMF at room temperature these values indicating that no conductive species are occur (24-26) .

Table (1) :The Optimal pH Values and wave length ($\lambda_{\max}$)with molar absorptivity (ϵ) of metal ions

	Metal Ions	Optimal pH	Optimal molar . conc X 10 ⁻³ mol	Molar obsorptivity X10 ³ l.mol ⁻¹ cm ⁻¹	optimal wave length (λ_{max})	Conductivity s.mol ⁻¹ .cm ²	B. mol ⁻¹ .L	Log B
No ₂ (BTADI)	Zn(II)	6	1-25	1.72	525	1.44	1.933×10 ⁸	9.28
λ max = 471	Hg(II)	7	1.25	1	537	3.01	9.33 × 10 ⁷	7.97

the antimicrobial results were obtained concentration $1 \times 10^{-4} \text{ M}$.



Wave number (cm^{-1})

Fig 6 : IR spectrum of (6 – NO_2 BTADI – $\text{Hg}(II)$)

Calculation of Complexes Stability Constants:-

The stability y constants are found spectrophotometrically by measuring the absorbance of solution of the mixture of the ligand and metal ion at

Biological Effect :-

The biological activity test (27) was attained for azo compounds through measuring the strength of this compounds to resist the growth of a different species of bacteria . Conversely compound (6 – NO_2 BTADI) showed no activity against staph and complex $\text{Hg}(II)$ in activity against fermium . It should motioned that

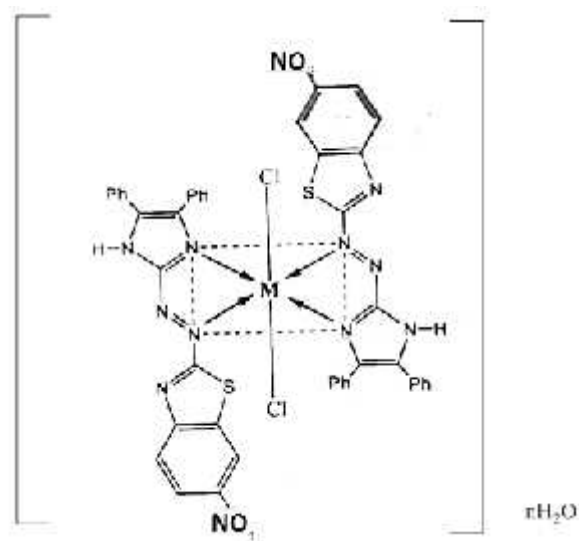
Table (2) : Anti bacterial activities of tested synthesized compound

	Staph	Asperacm	Fusrium	Ps
(6 – NO ₂ BTADI)	-	+	+	++
(6 – NO ₂ BTADI) Zn	+	+	++	+
(6 – NO ₂ BTADI) Hg	+	+	-	+

According to these results the following structure these complexes may be proposed .

Reference

1. Khool.M.K, Al-sharify.Abbas .N and Kasim. H. **2005**. Synthesis and spectrophotometric study of 4-(6-Nitro -2-benzothiazolyl azo) Resorcinal as Analytical Reagent for the Determination of zinic .J. Nat . of chem; 20:493-500 .
2. Carvalho.L.S,Spinola A.C, Ferreira S.L and Teixeira .L.S,**2004**. Spectrophotometric determination of Chromium in Steel with (TAR) using microwave radation ,J. Braz. Chem ;15 :1, 1-8 .
3. Katami .T, Hayakawa T ,Furukawa .M, Shhibata .S and Hara.T **.1986**. Spectrophotometric Study of some metal complexes with 2-[2-(3,5 –dibromopyridyl) azo] -



Hg n=1 , Zn n=1

Fig 7 : The suggested structural formula of Zn and Hg complex

- hydroxy phenyl)maleimide and N-(4-Methylphenyl)maleimide .J. Molecules. Chem;15: 7498-7508.
10. Al-adely.Khalid J.**2007**.Synthesis and Spectrophotometric study of Co,Ni and Cu Ions complexes with some new azo dyes containing 4,5-diphenyl imidazole. J. Nat. Chem;28 :585 .
11. Hofman. K.**1953**, " Imidazole and its Derivatives " Interscience . New York.
12. Asraa.N.K **.2015** , Ph.D.Thesis,College of Science , University Babylon.
13. Ewing. J.W.**1985**. " Instrumental Methds of Chemical Analysis " . McGraw- Hin.
14. Asraa.N.K and Sami .W.R.**2006**. Synthesis and spectral study of new imidazoleazo reagent 2-(2,4-dinitro phenyl azo)4,5-diphenyl imidazole with (IIB) metal ions ,J.Al-Qadisiah for pure Sci. Chem; 11(3):147-167.
15. Silverstein .R.M.**1996**. " Spectrometric Intentionification of organic compound "6th , Ed, Jhon Willey and Sons.
- 2-(2-Benzothiazolylazo) -5-dimethylaminobenzoic acid .J, Ana ,Chem , 2: 169.
4. Marczenko. Z.**1976**. Spectrophotometric determination of Elements .John Wiley and Sons ,New York.
5. Gavazov.K, Simenova.Z and Alexandrov.A.**2000**.Extraction Spectrophotometric determination of Vanadium in natural water .J. Talanta ,Chem, 52(3):539-544.
6. Swati, Singh. P, Karnwat. R, Sharma. I.K and Verma .P.S.**2011**. Synthesis, Electrochemical and Antimicrabial Studies of 2-phenylazo-1-naphthol-4-Sulphonic acid ,J.Internation (Indian). Chem.Tech. Res;3(3):1164-1171.
7. Al-Etaibil.A, El-Asasery. M .A and Kamel. M. M.**2015**. J. Int.Curr. Microbiol . App. Sci; 4(5): 923-928.
8. G.A.Tawfiq. **2013**. M.Sc. Thesis , College of Education of Pure Science Ibn-AlHaithem , M.Sc.University of Bagdad.
9. Issam. A.M and Asiza. M. **2010**. Synthesis of new azo compounds based on N-(4-

2010. Synthesis and Spectral Studies of some Transition Metal Complexes With New Thiazolylazo Ligand ,J.Nat ;38:311-324.
24. W.Mohmoud , G.G.Mohmad , M.M.I.El-Dessouky .**2014**. Int.J.Elect.Sci;9:1415.
25. M.K.Singh , R.Lasker , S.Sutradhar , B.Paul , S.Bhattacharjee, and A.Das, .**2014**, *IOSR J.Appl.Chem*; 7:4.
26. Skog , D.A.**1988**. " Fundamental at Analytical chemistry " 6th .Ed New york ;87:24411.
27. Prez.C, Pauli.M and Bazerque.P.**1990**.An antibiotic assay by the ager –well diffusion method ,J. Actabioloie, Chem; 15:(113-115).
16. Asniza. M, Issma .A.M and Abdeul Khalil. H.P.**2011**. Synthesis and characterization of anew Hetrocyclic azo pigment, J.Sains Malaysiana. Chem; 40(7):7498- 7508.
17. Ballamy .L.J.**1975**. Infra- Red Spectra of complex Molecules , Champman and Hall, 3td .Ed.
18. Abdil Allah. M, Mathak. S and Kudhair. H . **2007**. Synthesis and Structural phenyl)azo]-4,5-diphenyl imidazole as new ligand,J. Al- Qadisial for pure Sci . Chem; 12(2):133-139.
19. Nakamoto . K.**1997**. "Infrared and Raman Spectra of inorganic and coordination compounds , New York , 3rd. Ed.
20. F.Karipcin , B.Dede , S.P.Ozkorucuklu , and E.Kabalciliar.**2010** .J.*Dyes and Pigments* ; 1:85.
21. K.R.Raghavendra , and K.A.Kumar . **2013**. *Int.J.Pur.Chem.Bio.Sci.* ;3: 2.
22. Al-Ghabsha. T.S and Al-Abachi. M.Q.**1986**. "Fundamentals of Analytical chemistry ".
23. Khalid .Jawad Al-adely,Abid Allal.M.A and Rahim.T.M.

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