Synthesis and Spectral Study of new Tetradentate Azo-Azomethine ligand as a drevitave of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions

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Abstract:

A new azo ligand N¹Z, N²Z) N¹,N²-Bis ((E-4,5-Di phenyl-1H – imidazole-2-yl)diazenyl) 1,5-di methyl-2-phenyl -1H-pyrazole-3-(2H)-ylidene) ethan-1,2-diimine (BDIDE) prepared by coupling reaction between 4,5-diphenylimidazole and 1,2- Bis –(4'-Amino-2',3'-Di methyl-1'-Phenyl- pyrazolinyl)-Diimino Ethan , The structure of ligand , mode of bonding, and overall geometry of it's complexes with Co(II),Ni(II) ,Cu(II), Zn(II), Cd(II), and Hg(II) were determined through IR,UV-Vis. ,¹H-NMR , and Mass spectral studies , magnatic momentum , elemental analysis , and Molar conductance , also the stability constants of the complexes were calculated geometry for all complexes in which a ligand was a bidentate and coordinated with metal ions through N(3) imidazole and one of nitrogen atoms of azo group spectrophotometrically, These studies revealed octahedral .

Key Wards:

Spectral study, Transtion metal complexes, Azo-Shiffe base, imidazole, azo.

Introduction :

Azo dyes are versatile compounds take large part of attention in research areas in both of fundamental and application, such as textile, leather, plastics, biological staining, lasers, cosmetics, and drugs (1).

Stability of Azo days, ease of synthesis, and ability to form a colored complexes with a various metal ions in solutions as well their interesting electronic and geometrical features give these compounds an important role in coordination field⁽²⁾.. Azoimidazole compounds were found to be a available to determinate many of metal ions, the heterocyclic nitrogen atom in imidazole ring is a vital part science it improved the chelation properties ⁽³⁾. by containing azoimine system (-

N=N-C=N-) thence they have the ability to coordinate with metal ions in their different oxidation states ⁽⁴⁾..

Azo-Shiffe base ligands which are contain azo (-N=N-) and azomethine (-C=N-) groups considered as π - accepter ligands where have a capability to stabilize metal ions in their low oxidation states ⁽⁵⁾. The coordination of these compounds can be acquired from one of these groups⁽⁶⁾. To by one of them ⁽⁷⁾...

In this work we are synthesis of new azo-shiffe base ligand as a derivative of 4,5- diphenyl imidazole and sex new chelat complexes with Co, Ni , Cu , Zn, Cd , and Hg divalent ions , and characterization the ligand and It's complexes by using different techniques .

Materials and Methods:

All chemicals were from Fluka , Meck , and B.D.H with high purity. Stuart melting point /SMP30 used to measure melting point of ligand and it's complexes , Element analysis of ligand carried out by CHN element analyzer 1108 and Element analysis of complexes measured by C.H.N.S. mth EA 99 Atomic H-NMR of ligand recoded by using Burker Ultra Sheild (300MHz) by using TMS as a internal standard for calibrating chemical shift of HNMR spectrum.

Electronic spectra in ethanol were recorded by Shimdzu 1800 double beam Spectrophotometer, FTIR spectra recorded 8400,s Shimadzu double beam with KBr disk, MSB –MKI magnatic balance determine used in magnitic susceptibility measurements, while mass spectrum of ligand carried out by Shimadzu GCMS-QP2010 Ultra while mass spectra of Complexes measured by, Conductivity measurements carried out by using WTW Cond 730-Laboratory Condactivity meter -1(20-010), and pH measurements done by using WTW pH meter terminal 740.

Synthesis of Azo-azomethine ligand Synthesis of 4,5-di phenylimidazole:

Mixture of (2.1gm, 0.01 mol) of benzile (0.26 gm, 0.01 mol) hexamethylenetetramine, and (6 gm, 0.035 mol) of ammonium acetate were dissolved in (50) ml of glacial acitic acid, The mixture was refluxed for (1) hour, then the solution was cooled and (200) ml of water was added, The imidazole derivative and recrystallized using Ethanole 50%, The purity of this compound was evaluated by TLC, The percentage of yield (80%) and m.p is (219-231) 0 C. Scheme(1).

Synthesis of 1,2- Bis –(4'-Amino-2',3'-Di methyl-1'-Phenyl-pyrazolinyl)-Diimino Ethan⁽⁸⁾.:

The Shiff base was synthesized by condensation of 4- amino antipyrine (4.066 gm, 20 mmol) in (80) ml of ethanol and (0.5 gm, 10 mmol) of ethylene diamine, The mixture was refluxed for 2 hours, The yello solid precipitate of Shiff base was filterd, washed with distilled water, dried, and recrystallized from ethanol and finally preserved in desiccators, yield 75%, (m.p.195-197 °C), The preparation was shown in Scheme(2)

Synthesis of (N^1Z, N^2Z) $N^{1,}N^2$ -Bis ((E-4,5-Di phenyl-1H –imidazole-2-yl)diazenyl) 1,5-di methyl-2-phenyl -1H-pyrazole-3-(2H)-ylidene) ethan-1,2-diimine (BDIDE)

The Solution of Diazonuim salt was prepared as fellow: (4.305 gm, 0.01 mol) of 1,2- Bis –(4'-Amino-2',3'-Di methyl-1'-Phenyl- pyrazolinyl)-Diimino ethane was dissolve in mixture of (2) ml HCl Conc. and (28) ml distilled water and stirred for (15) min. in ice bath then ice cold solution of NaNO₂ (10%) (25) ml was add drop wise on a period of (30) min, the solution become yellowish orange and left for another (30) min, then add drop wise to another ice cooled solution of 4,5- diphenylimidazole (4.420 gm, 0.02 mol) in (25) ml of alkaline ethanol, The temperature mentioned below (5) °C during all processes and the solution color change to deep orange, add (200) distilled water and allowed to stand overnight, the precipitate was flittered washed with distilled water, dried in air and recrystallization from ethanol, yield (75%), m.p. (223-225) °C, Scheme (3)

Synthesis of complexses:

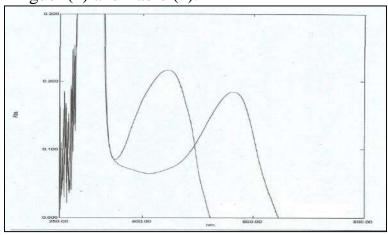
All complexes were prepared by adding ($0.456~\rm gm$, $0.001~\rm mol$) of ethanolic solution of the ligand to the ($0.0005~\rm mol$) of metal ion chloride salts in their proprate buffer solutions , The mixtures were stirred for 30 minutes , The precipitations of the complexes were flittered, washed with distilled water , dried over $CaCl_2$, and recrystallized from absolute ethanol , Table(1) show the physical properties of ligand and it's metal complexes.

Scheme (1): Synthesis of 1,2- Bis –(4'-Amino-2',3'-Di methyl-1'-Phenyl-pyrazolinyl)-Diimino ethane

Scheme (3): Synthesis of ligand (BDIDE)

Results and Discussion:

Electronic spectra of ligand show two absorption bands in Uv. region (220) nm due to π - π * transitions of aromatic rings thise band appeared also approximately in the same potions in complexes spectra , the second one appeared in (435) nm due to C.T transitions in Vis. region which is shifted to high wave lengths in complexes spectra as a result of (MLCT) as showed in Figuer (1) and Table (2).



Fig(1): UV-Vis. Spectra of ligand (BDIDE) and one of it's Complexes with Cu(II)

Table (1): Physical properties of ligand(BDIDE) and it's complexes

		M.P.	% of	Found (Calc.) %			
Compound	Color	(C0)	prod.	С%	Н%	N%	M%
(BDIDE)	Orange	220-	78	(72.62)	(5.42)	(21.96)	
C54H48N14		224		72.56	5.48	21.88	
Co (BDIDE) Cl ₂	Red	173-	65	(63.41)	(4.73)	(19.17)	(5.76)
$CoC_{54}H_{48}N_{14}Cl_2$		175		63.50	4.67	18.96	5.70
Ni (BDIDE) Cl ₂	Clarate	187-	71	(63.42)	(4.73)	(19.18)	(5.74)
NiC ₅₄ H ₄₈ N ₁₄ Cl ₂		189		63.53	4.68	19.12	5.70
Cu (BDIDE) Cl ₂	Dark	192-	75	(63.12)	(4.71)	(19.08)	(6.18)
$CuC_{54}H_{48}N_{14}Cl_2$	red	194		62.86	4.75	19.13	6.23
Zn (BDIDE) Cl ₂	Clarate	180-	68	(63.01)	(4.70)	(19.05)	6.35
ZnC54H48N14Cl2		182		63.07	4.65	18.92	6.28
Cd (BDIDE) Cl ₂	Purpel	168-	80	(60.26)	(4.49)	(18.22)	10.44
CdC54H48N14Cl2		171		60.34	4.52	18.17	10.35
Hg (BDIDE) Cl ₂	Clarate	155-	73	(55.69)	(4.15)	(16.84)	
$HgC_{54}H_{48}N_{14}Cl_2$		157		55.54	4.21	16.80	

<u>Table (2)</u>: Electronic spectra, conductivity, and magnetic moment of ligand (BDIDE) and it's complexes

Compound	Type of transition	λmax (nm)	Condactivity S. mol ⁻ .cm ⁻	μeff (B.M)
(BDIDE)	CT	453		(D.WI)
Co(BDIDE) Cl ₂	MLCT	461	8	4.70
Ni (BDIDE) Cl ₂	MLCT	464	10.5	2.82
Cu(BDIDE) Cl ₂	MLCT	535	18	1.73
Zn(BDIDE) Cl ₂	MLCT	556	12	Dia
Cd (BDIDE) Cl ₂	MLCT	530	10	Dia
Hg (BDIDE) Cl ₂	MLCT	562	7	Dia

Magnatic Susceptibility and Molar Conductance:

The magnetic moment values of Co(II), Ni(II), and Cu(II) suggested the Octahedral geometry of the complexes $^{(9-10)}$, while Zn(II), Cd(II), and Hg complexes are found to be diamagnetic as expected for d^{10} configuration, while the conductivity of 10^{-3} M of the complexes solutions in DMF at room temperature indicating the non-conductive character of them as shown in Table (2).

Infrared spectra

FTIR spectra of ligand showed absorption band in (3431.4) cm represented the stretching band of v(N-H) of imidazole ring (11-13) and it does not affected during the complexation , The same thing occur with the absorption band at (1655.20) cm $^-$ which assigned for v(C=N) of azomethine group in ligand spectra , there is no significant change in

position and intensity of this band in complexes spectra , that suggested the complexation does not occur through these group. The absorption band appeared in (1514.17) cm- in ligand spectrum refers to $\upsilon($ C=N) of imidazole ring which shifted to a lower frequencies in complexes spectra with a change in intensity , indicate the complexation can be occur through the non-bonding lone pair on nitrogen atom $^{(14-17)}$. The bands of $\upsilon($ N=N) group appeared in (1496.81) and (1452.45) cm- in ligand spectrum shifted to a lower frequencies in complexes spectra that indicated the azo group coordinated with metal ion $^{(18)}$. The two mono substituted aromatic rings on imidazole ring were indicated by the absorption at (761.91) and (698.25) cm- $^{(19)}$. Complexes spectra show new band in (500- 400) cm- region due to $\upsilon($ M-N) $^{(20)}$, as show in figures (2,3) of ligand and one of it's prepared complexes and listed in Table (3) .

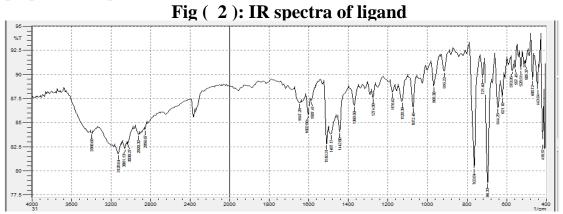


Table (3): Selected FTIR absorption band of ligand and it's complexes in cm⁻ units

Compound	υ(N-H)	υ(C=N)	v(C=N) imi.	υ(N=N)	υ(M-N)
(BDIDE)	3431.48	1655.20 w	1514w	1496.81m	
	wbr				
Co(BDIDE) Cl ₂	3431.48	1655.12 w	1510 m	1455 m	422 w
	wbr				
Ni (BDIDE) Cl ₂	3422.18	1656.00w	1512 m	1458 m	338 w
	wbr				
Cu(BDIDE) Cl ₂	3409.83	1655.20 w	1508 m	1449 m	412 w
	wbr				
Zn(BDIDE) Cl ₂	3430.23	1655.20 w	1510 m	1458 m	357 w
	wbr				
Cd (BDIDE) Cl ₂	3425.13	1655.42 w	1510 m	1567m	427 w
	wbr				
Hg (BDIDE) Cl ₂	3429.24	1655.20 w	1511 m	1542 m	436 w
	wbr				

Mass spectra

The mass spectra can be used to confirm the suggested structure of both ligand and it's complexes , the molecular ion of ligand appeared at(e/z =893) corresponding to the molecular formula ($C_{54}H_{48}N_{14}$) , while the base peak appeared in (e/z= 220) corresponding to 4,5- diphenylimidazole fragment ($C_{15}H_{12}N_2$) $^{(21)}$, The molecular peak of Ni(II) complex appeared in (e/z= 1022) with low m/z (less 1%) due to the large Mwt. of ligand corresponding to the [(NiC $_{54}H_{48}N_{14}$) - Cl $_2$] fragment and the base peak in (e/z= 220) which is related to [($C_{15}H_{12}N_2$)] fragment , The successive fragmentation of ligand and it's complex with Ni (II) ion were show in schemes (4) and (5)

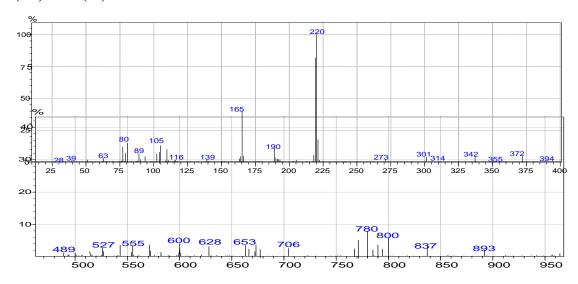
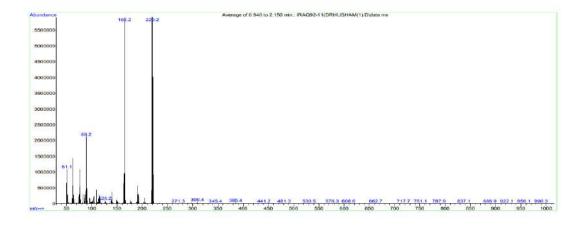


Fig (4): Mass spectra of ligand

Scheme (4): Mass fragmentation of ligand



 $Scheme(5): Mass\ fragmentation\ of\ Ni\ (II)\ complex\ with\ ligand\ HNMR\ Spectra$

HNMR spectrum of ligand in DMSO showed signals in σ (12.49) ppm due to (N-H) proton of imidazole ring ⁽⁷⁾, multiples of aromatic protons in σ (7.50- 7.19) ppm ⁽²⁰⁾, while three signals in σ (2.80) ppm due to (-C –CH₂-C-) protons , while the other two signals at σ (2.50) ppm and σ (3.37) ppm due to (-C-CH₃) and (-N-CH₃) of pyrazole ring as shown in figure (6).

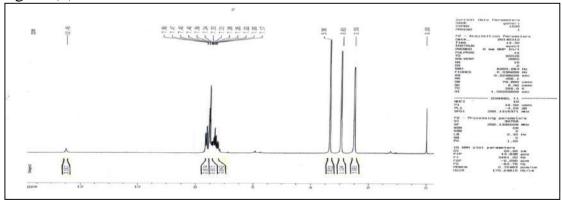
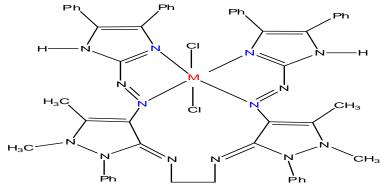


Fig.(6): HNMR Spectra of ligand

Mole Ratio showed that , all complexes are prepared in(1:2) (M:L) . The Stability Constants for prepared complexes were calculated spectrophotometrically and found that the Stability Constants were varied in the arrangement $\text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$ which agree with Irving – Williams Series , as show in Table (4)

Table(4): Stability Constant values of (BDIDE) and it's Complexes

Compound	α	K	Log K	
Co(BDIDE) Cl ₂	0.023	3.078×10^{7}	7.488	
Ni (BDIDE) Cl ₂	0.013	8.520×10^{7}	7.930	
Cu(BDIDE) Cl ₂	0.011	11.620×10^7	8.065	
- " (
Zn(BDIDE) Cl ₂	0.020	4.083×10^{7}	7.611	
Cd (BDIDE) Cl ₂	0.027	2.070×10^{7}	7.316	
` ′				
Hg (BDIDE) Cl ₂	0.034	1.341×10^{7}	7.127	



M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II)

Fig. (7): The proposed structure of the complexes

References:

- 1- F.Karipcin, E. Kabalicar, Acta Chem. Solv., **2007**, 54, 242 247.
- 2- C.J.Athira , Y. Sindhu , M.S. Sujmol , K.Mohanan , J.Serb Chem.Soc. , **2011** , 76 , 249-261.
- 3- A.A.Fadda, K.M.Elatter, American Journal of Organic Chemistry, **2012**, 2, 52-57.
- 4- R. Hrdina, D. Lustinec, P. Sotolin, L. Lunak, M. Holcapek, Advances in Color Sience and Technology, **2004**, *7*, 5-17.
- 5- L.Lai, Y.Ging Yang, L.Wung, Jwu Wang, Journal of the Chinese Chemical Society, **2005**, 52, 1201-1204.
- 6- A.J.Jarad , M.A.Kadhim , and S.A. Jabrallah , J.Bagdad for Sci. , **2012** , 9, 178-186 2012.

- 7- S.Patai, The Chemistry of Hydrazo, Azo, and Azoxy Groups, 2 nd, (Jhon Wielly and Sons, 1997), 105.
- 8- H. Kumar, and R. P. Chaudhary, Der Chemica Sinica, **2010**,1, 55-61.
- 9- H. H. Eissa, Journal of Current Research in Science, **2013**, 1, 96 103.
- 10- A.W. Naser, H.T. Ghanem, A.M. Ali, J.of University of Anbar for Pure Science, **2010**, 4,
- 11- N.Kurtoglu, J.Serb.Chem.Sec., 2009, 74, 917-926.
- 12- A.A-Al Hamdani, S.A. Shaker, Oriental journal of Chemistry, **2011**, 27, 835-845.
- 13- P.Byabartta, African journal of pure and applied Chemistry, **2009**, 3, 177-182.
- 14- S.K.Jawad, Z.A.Mutalib, Journal of Thi-Qar University, **2010**, 5, 25-39.
- 15- N.Raman, S.Ravichandran, C.Thangaraja, J.Chem.Sci., **2004**, 116, 215-219.
- 16- S.O.Podunavac, V.M.Leovac, G.S. Cetkovic, S.L.Markov, Apteef, **2002**, 33, 151-157.
- 17- S.A.Al-Sabaawi, College of Basic Education Researches Journal, **2011**, 11, 35-42.
- 18- P.Naumov, G.Jovanoviski, Acta. Chim.Solv., **1999**, 461, 389-404.
- 19- B.Das, M.R. Reddy, N.Ravinranathy, K.H.Kishore, U.S.Murthy, Indian Journal of Chemistry, **2005**, 4413, 1119-1120.
- 20- S.Dutta, Acta.Pharm., 2010, 60, 229-235.
- 21- S.Karim, Journal of Babylon University Pure and Applied Science, 2011, 1, 56-62.
- 22- A.M.Ali, National Journal of Chemistry, 2010, 37, 66-73.
- 23- B. Kirikan, R. Ramazan, Turk. J.Chem., 2008, 32, 9-17.
- 24- A.M.Ali , D.N.Taha , A.A.Alkurymy , A.Saadon; National Journal of Chemistry, **2008** , 31, 383-393.
- 25- R.T.Mehdi , and A.M.Ali ; National Journal of Chemistry, **2005** , 20 , 540-546.
- 26- P.Govindaswamy , Y.A.Mozhariviskyj , M.R.Kollipara , Polyhydron, **2007** , 26 , 5039-5044 .
- 27- E.Chauveau, C. Marestin, F.Schiets, and R. Mercier; Green Chem., 2012, 12, 1018-1022.
- 28- Ak. Kaura , M.Kaura , Interntional Journal of Chemical and Pharmaceutical Scinces, **2012**, 3,24-28.

الخلاصة:

تم تحضير الليكاند الجديد N^2 , N^1 (N^2 Z, N^1 Z) – ثنائي فنيل أميدازول – -2 – يل - دايازانيل) -5 – ثنائي مثيل – -2 – فنيل —بايرازول – -2 – يل دايين) إيثان – -2 – ثنائي الأيمين (BDIDE) بواسطة تفاعل الأزواج بين المركبين -5,4 – ثنائي فنيل إميدازول والمركب -21 – ثنائي -21 أمينو – -22 ، -23 – ثنائي مثيل – -1 – بايرازولينايل -11 – ثنائي أيمينو إيثان والمركب -12 – تنائي (-14 – أمينو – -15 – ثنائي مثيل – -14 – بايرازولينايل -15 – ثنائي أيمينو إيثان آمو (-14 – أمينو إيثان (-14 – أمينو إيثان (-14 – أمينو إيثان (-15 – أمينو إيثان (-15 – أمينو إيثان (-16 – أمينو إيثان (-18 – أمينو إيثان (-19 – أمينو أيونات المخاب أمينو المعقدات المحضرة مع الليكاند والذي يتناسق كليكاند ثنائي المخلب الشكل الثماني السطوح لجميع المعقدات المحضرة مع الليكاند والذي يتناسق كليكاند ثنائي المخلب مع الأيونات المدروسة من خلال ذرة نتروجين رقم (-18) لحلقة الأميدازول وذرة نتروجين مجموعة الآزو البعيدة عن الحلقة غير المتجانسة.

²⁹⁻ B.M. Dinnimath, S.M.Hipparagi, Y.M. Gowda, Research J. Pharm. and Teach., **2011**, 4, 1413-1417.

³⁰⁻ J. Liu, B.Wu, B.Zhang, Journal of Chinese Chemical Society, **2005**, 52, 1165-1170.