Synthesis of new azo imidazole ligand and fabricating it’s chelate complexes with some metallic ions

Husham M. Hasan Mubark*1, Israa N.Witwit2, Abid Allah M. Ali3
*1,2 Dept. of Chemistry, Faculty of Science, University of Kufa
3 Dept. of Chemistry, College of Education For Women, University of Kufa

hushamhassan1974@gmail.com

Abstract. New ligand (TBPAM) was synthesized by coupling between (4-tetra-butyl)aniline and 4-methyl imidazole, then studied it’s coordination behavior with five metal ions Co(II), Ni(II), Cu(II), Cd(II), and Hg(II), the ligand (TBPAM) and the prepared complexes were characterized by using Mass, 1HNMR, Ultra violet-visible, FT-IR, Magnetic susceptibility and also by Molar conductivity. The conclusion of the data indicated the octahedral geometry of the complexes that have general formula \([M(TBPAM)\_2Cl_2]\), where the ligand (TBPAM) behave as bidentate from azo group and imidazole moiety.

Keywords. 4-methylimidazole, azo, complexes, azo imidazole.

1. Introduction
Imidazole azo compounds obtained researchers interesting due to the chemical characters of imidazole ring which has a mixture properties between pyrimidine and pyrole rings that increased their thermal stability and colorimetric sensitivity [1, 2, 3], as well as their importance in a different academic and applied fields especially in coordination chemistry as they well known as bidentate ligands [4], sometimes they are coordinated as tri and tetradentate ligands through additional coordination sites which found on the other ring that connected to the azo group [5]. Imidazole azo and their alternative azo imidazole ligands showed an ability to coordinate with many of metal ions in their low oxidation state due to the ability of imidazole moiety \(\pi^*\) orbitals to receive back donation electrons from the metallic center which increased the stability of these complexes [6, 7].

Continuation with our previous work the researchers aimed to prepare a new azo imidazole ligand as a derivative of 4-methyl imidazole, and synthesis a series of it’s chelate complexes with Co(II), Ni(II), Cu(II), Cd(II), and Hg(II) ions, characterized these complexes with different techniques such as Mass, 1HNMR, IR, Uv-Vis, Magnetic susceptibility, and Molar Conductivity.

2. Materials and Methods

2.1. Chemicals and Instruments
All chemical compounds used were from, BDH., Merck, and Sigma Aldrich companies.
Mass spectrum executed by AB Sciex 3200 Qtrap Mass analyzer, FT-IR measured by Bruker, Electronic spectrum recorded by Shimadzu UV-1800 Spectrophotometer, while the element analysis were obtained by Costech ECS Elemental 4010, Balance Magnetic Susceptibility Model –M.S.B Auto used to measure the magnetic susbtibility of the complexes, whereas molar conductivity was carried out by 720(WTW), and $^1$H NMR recorded by Bruker Avance-111 300 MHz NMR Spectrometer.

2.2. Preparation of (TBPAM) Ligand

Free ligand (TBPAM) was prepared by mixing (10 mmole, 1.58 ml) of (4-tetra-butyl) aniline with (3) ml of hydrochloric acid in (25) ml of distilled water in an ice bath (below 5°C), then cold solution of sodium nitrate (0.71 gm of NaNO₂ in (10) ml of distilled water) was added to this solution drop by drop with continuous stirring and left it for (30) min to complete formation of diazonium salt.

The diazonium salt solution was added gradually to an alcoholic solution of 4-methyl imidazole which prepared by dissolving (10 mmole,0.82 gm of 4-methyl imidazole in 25 ml of ethanol and 15 ml of 10% NaOH aqueous solution ) in the ice bath , The orange color were appeared left for 24 hours ,neutralized with diluted HCl, filtered , and dried then recrystallized from hot ethanol , Scheme(1) show the ligand synthesis pathway:

![Scheme 1. Preparation of (TBPAM) ligand](image)

2.3. Preparation of the (TBPAM) complexes

All complexes of (TBPAM) were prepared with mole ratio (1:2) (M:L) by adding with continues stirring (10) ml of distilled water containing (10) mmole of each metal ion chloride (separately ) to (20) ml of ethanolic solution (20) mmole of ligand (TBPAM) drop by drop until the precipitations of complexes were appeared , posteriorly filtered , dried, and recrystallized from hot ethanol , some physicochemical properties of (TBPAM) ligand and it’s chelate metal ion complexes showed in the table (1) and scheme (2) represented metal complexes formation pathway:

![Scheme 2. Preparation of (TBPAM) complexes](image)
Table 1. Values of Physicochemical properties of (TBPAM) ligand and it’s complexes

| Compound          | M.wt | Product (%) | Color   | Elemental Analysis Calculated (Found) | m. p (°C) |
|-------------------|------|-------------|---------|--------------------------------------|-----------|
|                   |      |             |         | C%   H%   N%                          |           |
|                   |      |             |         | Theoretical | Calculated | Found   | |
| (TBPAM) C₁₄H₁₈N₄ | 242.1| 73          | Orange  | 69.39(69.22) | 7.49(7.51) | 23.12(23.16) | 131-133  |
| Co(TBPAM)₂Cl₂   | 614.4| 82          | Brown   | 54.73(54.74) | 5.91(5.88) | 18.24(18.26) | Dec.<25   |
| C₂₅H₂₈Cl₂CoN₆  | 614.2| 72          | Brown   | 54.75(54.71) | 5.91(5.96) | 18.24(18.21) | 166-168   |
| Ni(TBPAM)₂Cl₂   | 619.1| 77          | Violet  | 54.32(54.35) | 5.86(5.88) | 18.10(18.07) | 190-192   |
| Cu(TBPAM)₂Cl₂   | 667.9| 84          | Red     | 50.35(50.31) | 5.43(5.46) | 16.78(16.76) | 177.5-    |
| C₂₅H₂₈Cl₂CuN₆  | 656.1| 83          | Red     | 44.48(44.50) | 4.80(4.77) | 14.82(14.85) | 181-183   |
| Cd(TBPAM)₂Cl₂   | 756.1| 78          | Red     | 44.48(44.50) | 4.80(4.77) | 14.82(14.85) |

3. Result and Discussion

Mass spectrum approved the formation of (TBPAM) ligand by showing the fragment at m/z (243) which agreed molecular formula and represented the molecular peak (M+1), the fragmentation of this ligand take place through two paths, the first path represented by loss of methyl group then losing azo group as (-N₂) molecule, the second path is started by dichotomy of azo group, mass spectrum of Co(II) complex also agreed with its molecular formula at m/z (614) as explained in figures (1, 2), and schemes (3, 4).

Figure 1. Mass Spectrum of (TBPAM) ligand
Chemical Formula: C$_{14}$H$_{18}$N$_{4}$

$\text{m/z} = (242 +1) \quad 25\%$

Chemical Formula: C$_{13}$H$_{16}$N$_{4}$

$\text{m/z} = (228 ) \quad 15\%$

Chemical Formula: C$_{13}$H$_{16}$N$_{2}$

$\text{m/z} = (200 + 1) \quad 20\%$

Chemical Formula: C$_{10}$H$_{15}$N

$\text{m/z} = (149 ) \quad 40\%$

Chemical Formula: C$_{9}$H$_{8}$N$_{2}$

$\text{m/z} = (144 +1) \quad 100\%$

Chemical Formula: C$_{7}$H$_{9}$N

$\text{m/z} = (107) \quad 7\%$

Scheme 3. Mass fragmentation of (TBPAM) ligand

Figure 2. Mass spectrum of Co(II) complex
Scheme 4. Mass fragmentation of Co(II) complex

The $^1$HNMR is an important tool to prove the structure of organic compounds, the signal appear at (1.33) ppm related with (CH$_3$)$_3$C protons while the signal at (2.6) ppm due to protons of Methyl group attached with Imidazole ring. The singlet at (7.10) ppm attributed with proton attached with carbon number (5) in imidazole ring while the multiplet (7.51 - 7.89) ppm due to the aromatic protons. The (-NH-) proton of imidazole ring have a weak signal at (12.81) ppm [8] as shown in figure 3.
Infra-Red spectrum of free ligand (TBPAM) between (600-4000) cm\(^{-1}\) showed a peak of \(\nu\) (N-H) of imidazole ring at (3420) cm\(^{-1}\) that did not show any change of position in the spectra of the complexes, while the peak of \(\nu\) (C=\(\text{N}\)) of imidazole ring \([9, 10]\) and \(\nu\) (N=N) group \([11, 12]\) at (1577)cm\(^{-1}\), and (1428) cm\(^{-1}\) respectively suffered from a change in both of position and intensity in the complexes due to participation of these groups in the coordination process the increasing in wavenumbers of these two groups in complexes due to increase the multiple bond property, table 2 showed the important peaks of FTIR for free ligands and its complexes:

### Table 2. FTIR wavenumber values (cm\(^{-1}\)) of ligand and its complexes

| Compound               | (TBPAM) | Co(II) Complex | Ni(II) Complex | Cu(II) Complex | Cd(II) Complex | Hg(II) Complex |
|------------------------|---------|----------------|----------------|----------------|----------------|----------------|
| \(\nu\) (C-H) of CH\(_3\) of imidazole ring | 3054 w  | 3056w          | 3056 w         | 3064 w         | 3057 w         | 3056 w         |
| \(\nu\) (C=\(\text{N}\)) imidazole | 1577 m  | 1591 m         | 1595 m         | 1592 m         | 1595 s         | 1592 m         |
| \(\nu\) (N=N)          | 1428 m  | 1461 m         | 1452 m         | 1460 m         | 1459 m         | 1407 m         |
| \(\nu\) (C-N) imidazole | 1374 m  | 1362 m         | 1346 m         | 1350 m         | 1348 m         | 1354 s         |

s: strong  m: middle  w:weak

UV-Vis spectrum of ligand (TBPAM) exhibit two bands at (368) nm, and (385) nm due to (n-\(\pi^*\)) and Intra ligand charge transfer toward hetero cyclic ring respectively, these bands suffered from bathochromic shift in the spectra of complexes accentual the coordination with metal ions ,Co(II) complex showed two bands at (384) nm and (501) nm for Intra ligand charge transfer(ILCT), and metal ligand (MLCT), while two bands of (ILCT) appeared at (389,439)nm and one band at (499) nm of MLCT in Ni(II) spectrum, Cu(II) complex showed three bands of (ILCT) at (204, 227, 387) nm and one band of (MLCT) at (472) nm, Cd(II) complex exhibit the (ILCT) bands at (236, 386 ) nm and (MLCT) at (492) nm, Finally Hg(II) complex gives two bands of (ILCT) at (230, 360) nm and one band at (508) nm for (MLCT), (d-d) transitions did not appeared in all of the complexes spectra, as shown in figures (4-6) and table (3).
The Conductivity measurements of the complexes in (DMSO) and (DMF) solvents indicated non-ionic character for all complexes[13], also the precipitate of AgCl was not observed after addition a drops of silver nitrate solution which confirms the absence of chloride as a counter ions out of the coordination sphere[14]. While the magnetic susceptibility agreed with the electronic configuration of each divalent metal ions and proposed the octahedral geometry [15] around the metal ions, as showed in table (3) and figure (7).

### Table 3. The data of Magnetic susceptibility, Molar Conductivity, and (Uv-vis) Electronic Transitions of ligand (TBPAM) and the prepared complexes.

| The Compound  | μ.eff. (B.M.) | Molar Conductivity S.Cm².mole⁻¹ | λ max (nm) | Type of Transitions | The Geometry   |
|---------------|--------------|---------------------------------|------------|---------------------|---------------|
| (TBPAM)       | -----        | -----                           | 368        | n-π*                | -----         |
| Co(II) Complex| 4.73         | 19.8                            | 385        | ICT                 | Octahedral    |
|               |              |                                  | 384        | ILCT                |               |
|               |              |                                  | 501        | MLCT                |               |
| Ni(II) Complex| 2.84         | 19.6                            | 389        | ILCT                | Octahedral    |
|               |              |                                  | 439        | ILCT                |               |
|               |              |                                  | 499        | MLCT                |               |
|               |              |                                  | 204        | ILCT                |               |
| Cu(II) Complex| 1.72         | 18.4                            | 227        | ILCT                | Distorted octahedral |
|               |              |                                  | 387        | ILCT                |               |
|               |              |                                  | 472        | MLCT                |               |
8

Cd(II) Complex | Dia | 24.4 | 22.8 | 236 | ILCT | Octahedral | ILCT | 386 | ILCT | MLCT | 492 | ILCT | 230 | ILCT | Octahedral | 333 | ILCT | MLCT | Octahedral |

Hg(II) Complex | Dia | 21.7 | 20.5 | 360 | ILCT | Octahedral | 508 | MLCT | Octahedral | 333 | ILCT | MLCT | Octahedral | 230 | ILCT | Octahedral | 333 | ILCT | MLCT | Octahedral |

Figure 7. Suggested Structure of the complexes

4. Conclusion
From the above results the octahedral geometry of all complexes was suggested, and the coordination behavior of (TBPAM) ligand was deduced as a bidentate ligand which attached to metallic center from nitrogen (3) of imidazole ring and one nitrogen atoms of azo group to form five member ring between the ligand and metal ion.

References
[1] Avijit Pramanik, Arghya Basu, and Gopal Das, “Coordination assembly of p-substituted aryl azo imidazole complexes: Influences of electron donating substitution and counter ions”, Polyhedron, Volume 29, Issue 8, 2010, Pages 1980-1989, DOI: https://doi.org/10.1016/j.poly.2010.03.022.
[2] Mamdouh, S.M., Swasan, S.H., Alaa E. A., and Nessma, M. N., “Synthesis and spectroscopic characterization of gallic acid and some of its azo complexes.” J. Mol. Struct, 2012, 1014, pp: 17-25.
[3] P. Byabartta, “Ruthenium azo complexes: Synthesis, spectra, and electrochemistry of dithiocyanato-bis[1-(alkyl)-2-(arylazo)imidazole]ruthenium(II)”, Russian Journal of Coordination Chemistry, Volume 35, Issue 9, 2009, pp 687–691.
[4] Sh. M. Eassa, “Spectrophotometric determination for chromium (III) and cobalt (II) with 4-(nitrophenyl azo imidazole) (NPAI) as organic reagent”, Journal of Chemical and Pharmaceutical Research, 2016, 8(8):85-92.
[5] Israa Noor Witwit, and Hussien Abd-mohamad “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 “journal of the college of basic education 22 (95),2016.
[6] Israa N. Witwit, Husham M. Mubark, Hutham Mahmood Yousif Al-Labban1, and Ahmed Abdul jabbar, “Synthesis and characterization of new imidazole azo ligand with some of transition metal ions, and their biological effect on two pathogenic bacteria of burn patients Int. J. Res. Pharm. Sci., 10(3),2019, 1847-1856, DOI: https://doi.org/10.26452/ijrps.v10i3.1382.
[7] Waleed A. Mahmoud, Abid Allah M. Ali, and Tamara A. Kareem, “Preparation and Spectral Characterization of New Azo Imidazole Ligand 2-[2’-Cyanophenyl Azo]-4,5-Diphenyl Imidazole and its Complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg (II) Ions “,Baghdad Science Journal, Vol 12 No 1 (2015): issue 1, DOI:
https://doi.org/10.21123/bsj.2015.12.1.96-109.

[8] Raheem T. Mahdi, Abid Allah M. Ali, and Huda A. Noaman, “Preparation and Characterization of Some Metal Complexes with New Heterocyclic Schiff-Azo Ligand”, Journal of Al-Nahrain University Science, Vol. 71 (4), December, 4174, pp. 17-18.

[9] Khalid J. Al-Adilee, and Haitham K. Dakheel, “Synthesis, Spectral and Biological Studies of Ni(II), Pd(II), and Pt(IV) Complexes with New Heterocyclic ligand Derived from Azo-Schiff Bases Dye”, Eurasian J Anal Chem 2018;13(5):em64, DOI: https://doi.org/10.29333/ejac/97267

[10] Alyakhider Abbas, and Rafal Salam Kadhim, “Preparation, Spectral and Biological Studies of Azo Ligand Derived from Proline with Cu(II), Ag(I) and Au(III) Metal Ion”, IOSR Journal of Applied Chemistry (IOSR-JAC), Volume 9, Issue 8, 2016, PP 20-31.

[11] Thanaa J. Al-Hasani, and Zainab S. Almaliky, “New Pd and Pt Complexes of Guanine –Azo Dye: Structural, Spectroscopic, Dyeing Performance and Antibacterial Activity Studies”, Iraqi Journal of Science, 2015, Vol 56, No.4A, pp: 2718-2731.

[12] Khalid J. Al-Adilee, and SAAD A. Atyha, “Synthesis, Spectral, Thermal and Biological Studies of Some Metal Complexes Derived from Heterocyclic Mono Azo Dye Ligand 2'(2'-Hydroxy-4-methyl phenyl)azo]imidazole”; Asian Journal of Chemistry; Vol. 30, No. 2 (2018), 280-292.

[13] Khalid J. Al-Adilee, Hussein A. K. Kyhoiesh, Preparation and Identification of Some Metal Complexes with New Heterocyclic Azo Dye Ligand 2-[2''- (1- Hydroxy -4- Chloro phenyl) azo ]- Imidazole and their Spectral and Thermal Studies, Journal of Molecular Structure, 2017; DOI: https://10.1016/j.molstruc.2017.01.054.

[14] Israa N.Witwit, Zahraa Y. Motaweq, and Husham M.Mubark,” Synthesis, Characterization, and Biological Efficacy on new mixed ligand complexes based from azo dye of 8-hydroxy quinoline as a primary ligand and imidazole as a secondary ligand with some of transition metal ions”, J. Pharm. Sci. & Res. Vol. 10(12), 2018, 3074-3083.

[15] Saad M.Mahdi, and Abdudallah M.Ali, “Preparation &identification of new azo-schiff ligand with its complexes”, Iraqi National Journal of Chemistry 2015; 15(2).