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Preparation, Characterization of Mixed-Ligand Complexes for Some Divalent Transition Metal Ions Involving Biologically Important Bidentate Ligands

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Abstract

This paper describes the synthesis, characterization of mixed ligand complexes. The reaction of benzene-1,2-diamine(*o*-phenylenediamine) derivatives with anthranilic acid (Ant) yield 2-(1*H*-benzimidazol-2-yl)aniline derivatives (BIAD) as (primary ligands) in Effective and appropriate solvent, which confirmed by FT-IR, Elemental analyses (C. H. N, O) and ^{1}H NMR spectral. These ligands coordinated with some transition metal ions (Co^{II} ,Ni^{II}, Cu^{II}, Zn^{II}) and anthranilic acid as (secondary ligand) at the (1 : 1 : 1) ratio of the components to yielded a mixed-ligand complexes. All complexes have been studied by IR spectra, ^{1}H NMR, Elemental analyses (C. H. N. O), atomic absorption, molar conductivity and magnetic moment. Ligands produce chelates with (1;1;1) (metal; ligands; ligand) interactive elements. From all results was suggested that octahedral geometry to complexes and have the formulae $[M(BIAD)(Ant)(H_2O)_2]^{2-}$ where M = $Co^{(II)}$, $Ni^{(II)}$, $Cu^{(II)}$ and $Zn^{(II)}$.

Keywords: Mixed-Ligand; anthranilic acid; BIAD; Benzimidazole.

1. Introduction

Benzimidazole is a moiety which contains benzene ring and a heterocyclic imidazole ring. Benzimidazole derivative are an important category of bioactive molecules in the domain of drugs and pharmaceuticals [1]. 2-Substituted analogs of benzimidazoles have very wide range of biologically active compounds, Anti-inflammatory activity [2,3], anti fungi and bacteria[4], antiviral[5], anti-hypertensive[6], human glucagon receptor antagonistic[7], and anti-infective [8] activities. 4-nitro-*o*- phenylenediamine ligand have a wide used in the synthesis of compounds with biological activities, like Quinoxaline [9], one of the other uses of 4-nitro-*o*-phenylenediamine ligand is in the Determination of Diacetyl in Beer [10].

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Anthranilic acid is one of important compounds that have widely biological activity, as an important precursor of tryptophan. Anthranilic acid is used with some mono oxidation metals to studies the demeanor of potassium in the biological systems [11]. Complexes that anthranilic acid contain ligand have extensive biological activity, anti-inflammatory activities[12], antibacterial[13].

The synthesis of a new mix-ligand complexes was a probably the most significant step in the evolution of metal complexes which offer unique properties and new reactivity. Mixed-ligand complexes (anthranilic acid) can inhibit the DNA interactions, and cytotoxicities[14]. Previously study show that the complexes of Rh with anthranilic acid and N-phenyl anthranilic acid can act as catalysts for hydrogenation [15], Terbium(III) complexes of anthranilic acid can appear the photoluminescence properties[16], a model into a peroxidase inhibitor complex[17].The complexes of metals ion with tow differences kinds of bioligands, as a heteroaromatic nitrogen bases may be present the importing biochemical interactions in different ways[18].However, the ligand of anthranilic acid have no anti-inflammatory activity, but it have ability to exhibit activity because of certain binding of $Cu^{(II)}$ ions at inflammatory locations [19]. Anthranilic acid ligand bidentate and bonding to the metals through the ionized carboxyl group and N amine atom [20]. In this work a several of mixed-ligand complexes of $Co^{(II)}$, $Ni^{(II)}$, $Cu^{(II)}$ and $Zn^{(II)}$ containing anthranilic acid (Ant) as secondary ligand and 2-(1*H*-benzimidazol-2-yl)aniline derivatives as primary ligands was synthesized and characterization.

2. Experimental

2.1. Materials and measurements

Metals, anthranilic acid (Ant) and all o-phenylenediamine derivatives are provide from BDH and Sigma Aldrich companies were used without purification. Melting points was registered by using digital Stuart scientific SMP30. Infrared Spectra Measurements was registered by FT-IR-8400S – SHIADZU by using KBr discs. ^{1}H-NMR spectra was registered on Burker 500MHz device by employing dimethyl solfoxide-d_6 and TMS. TLC were implemented all over ligand reactions by (Gelman sciences LTD. U.K.). (C, H, N, O) analysis data was gained by employing a EA 3000 analysis instrument, (Co^{II} ,Ni^{II}, Cu^{II}, Zn^{II}) were determined by atomic absorption technique using Shimadzu AA-6300.

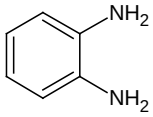
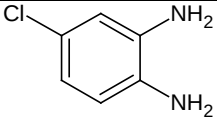
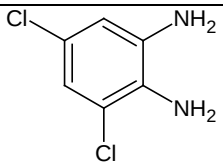
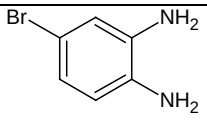
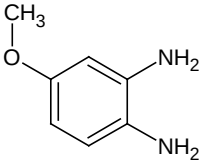
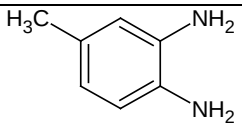
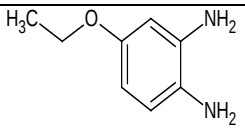
The complexes diagnoses by using Magnetic susceptibilities was specified by Sherwood Scientific's Magnetic Susceptibility Balances. Molar conductance of the Mixed-Ligand Complexes was detected in DMF using conductivity meter Alpha-800 in (25 $^{\circ}$C, 10^{-3} mol L^{-1}).

2.2. General methods to prepare the 2-(1H-benzimidazol-2-yl)aniline derivatives (BIAD) ligands

Mixture of (0.03 mole, 6.27g) anthranilic acid, (0.03 mole) *o*-phenylenediamine derivatives, 50 ml dioxane were reflex for 1 hour in water bath.

The concentration ammonia solution was graduated addition to mixture. The precipitate collected and recrystallized with C_2H_5OH to produce crystals. The Physical features of ligands are recorded in (table 1).

Table 1: Physiochemical properties of ligands (BIAD) (1a-g).

Comp.	*o*-ph.diam. derivatives	Mol. formula	Mol. Wt.	M.P.	% yield	colour
1a		$C_{13}H_{11}N_3$	209.24	85–87	72.68	gray
1b		$C_{13}H_{10}ClN_3$	243.69	106-108	76.30	Pale Yellow
1c		$C_{13}H_9Cl_2N_3$	278.13	218-220	84.00	yellow
1d		$C_{13}H_{10}BrN_3$	288.14	225-227	76.84	Dark brown
1e		$C_{14}H_{13}N_3O$	239.27	231-233	55.5	gray
1f		$C_{14}H_{13}N_3$	223.27	166-169	53.76	Orang
1g		$C_{15}H_{15}N_3O$	253.29	204-206	52.12	Colorless

2.3. preparing of 2-(1H-benzimidazol-2-yl)aniline (1a)

Were prepared from anthranilic acid and o- phenylenediamine; (^{1}H-NMR) : 12.49 (s, 1H, H-N), 5.0 (s, 2H, NH2), 6.49–6.50 (dd, Phen-H), 6.34–6.38 (dd, Phen-H), 7.84–7.83 (d 1H, Phen-H), 7.12– 7.14 (d, 1H, Phen-H), 7.39–7.41 (m, 2H, Phen-H), 7.59–7.63 (d, 1H, Phen-H). IR (υ, cm-1): 3420-3427 (-NH2), 3358 (-NH), 1618 (C=N). (Calcd.). Found, to C13H11N3 (209.25): C (73.61) H (6.29) N (21.10)%. Found: C 73.79; H 6.44; N 21.89%.

2.4. Synthesis of 2-(6-chloro-1H-benzimidazol-2-yl)aniline (1b)

Was Synthesis from anthranilic acid and 4-chlorobenzene-1,2-diamine; (^{1}H-NMR): 11.97 (s, 1H, H-N), 5.82 (s,

2H, NH2), 7.36 (s, 1H, Phen-H), 8.51 (d, 1H, Phen-H), 7.14 (d, 1H, Phen-H), 6.99 (d, 1H, Phen-H), 7.62 (d, 1H, Phen-H), 7.28 (t, 1H, Phen-H), 6.96 (d, 1H, Phen-H). IR (υ, cm^{-1}): 3420 - 3418 (- NH_2), 3410 (-NH), 1630 (C=N) 1046 (Ar-Cl). (Calcd.). Found, to $C_{13}H_{10}ClN_3$ (243.69): C (65.10) H (5.14) N (18.25) Found: C 65.11; H 5.18; N 18.23 %.

2.5. Synthesis of 2-(4,6-dichloro-1H-benzimidazol-2-yl)aniline (1c)

Was prepared from anthranilic acid and 3,5-dichlorobenzene-1,2-diamine; (^{1}H-NMR): 11.97(s, 1H, H-N), 5.78 (s, 2H, NH_2), 8.24 (s, 1H, Benzi-H), 8.28 (s, 1H, Benzi-H), 7.01 (d, 1H, Phen-H), 7.62 (d, 1H, Phen-H), 7.28 (t, 1H, Phen-H), 6.96 (t, 1H, Phen-H). IR (υ, cm^{-1}): 3420 - 3418 (-NH_2), 3412 (-NH), 1630 (C=N) 1110 (Ar-Cl). (Calcd.). Found, to $C_{13}H_9Cl_2N_3$ (278.13) : C(57.15) H(4.26) N(14.12) % Found: C, 57.12 ; H, 4.26; N, 14.13%.

2.6. Synthesis of 2-(6-bromo-1H-benzimidazol-2-yl)aniline (1d)

Was synthesis from anthranilic acid and 4-bromobenzene-1,2-diamine; (^{1}H-NMR): 12.10 (s, 1H, -HN), 5.79 (s, 2H, NH_2), 7.87 (s, 1H, Benzi-H), 8.46 (d, 1H, Benzi-H), 8.10 (d, 1H, Benzi-H), 6.99 (m, 1H, Phen-H), 7.62 (d, 1H, Phen-H), 7.28 (m, 1H, Phen-H), 6.96 (m,1H, Phen-H). IR (υ, cm^{-1}): 3419 - 3417 (- NH2), 3410 (-NH), 1631 (C=N), 1030 (Ar-Br). (Calcd.). Found, to $C_{13}H_{10}BrN_3$ (288.14) : C(55.20) H(4.50) N(13.51) % Found: C, 55.21 ; H, 4.52; N, 13.59 %.

2.7. Synthesis of 2-(6-methoxy-1H-benzimidazol-2-yl)aniline (1e)

Was prepared from anthranilic acid and 4-methoxybenzene-1,2-diamine ; (^{1}H-NMR): 12.55 (s, 1H, H-N), 5.78 (s, 2H, NH_2), 7.12 (s, 1H, Benz-H), 8.56 (d, 1H, Benz-H), 6.93 (d, 1H, Benz-H), 6.99 (m, 1H, Phen-H), 7.62 (d, 1H, Phen-H), 7.28 (m, 1H, Phen-H), 6.96 (m,1H, Phen-H), 3.87(s, 3H, methyl). IR (υ, cm^{-1}): 3420 - 3417 (-NH_2), 3408 (-NH), 1635 (C=N), 2844-2926 (C-H aliphatic). (Calcd.). Found, to $C_{14}H_{13}N_3O$ (239.27) : C(71.28) H(4.98) N(16.56) O(6.69) % Found: C, 71.30 ; H, 4.94; N, 16.60 ; O, 6.67%.

2.8. Synthesis of 2-(6-methyl-1H-benzimidazol-2-yl)aniline (1f)

Was synthesis from anthranilic acid and 4-methylbenzene-1,2-diamine ; (^{1}H-NMR): 12.56 (s, 1H, H-N), 5.79 (s, 2H, NH_2), 7.43 (s, 1H, Benz-H), 8.12 (d, 1H, Benz-H), 7.00 (d, 1H, Benz-H), 7.62 (m, 1H, Phen-H), 7.54 (d, 1H, Benz-H), 7.28 (m, 1H, Phen-H), 6.96 (m,1H, Phen-H), 2.42(s, 3H, methyl). IR (υ, cm^{-1}): 3421 - 3418 (-NH_2), 3411 (-NH), 1633 (C=N) 2840-2931 (C-H aliphatic). (Calcd). Found, to $C_{14}H_{13}N_3$ (239.27) : C(74.33) H(5.87) N(17.82) % Found: C, 74.36 ; H, 5.89; N, 17.80 %.

2.9. Synthesis of 2-(6-ethoxy-1H-benzimidazol-2-yl)aniline (1g)

Was synthesis from anthranilic acid and 4-ethoxybenzene-1,2-diamine ; (^{1}H-NMR): 12.11 (s, 1H, -HN), 5.79 (s, 2H, NH_2), 8.08 (d, 1H, Benz-H), 6.99 (d, 1H, Phen-H), 8.62 (d, 1H, Phen-H), 8.28 (m, 1H, Phen-H), 6.96 (m, 1H, Phen-H), 4.04 (s, 2H, methylene), 1.34 (s,3H, methyl). IR (υ, cm^{-1}): 3421 - 3415 (- NH_2), 3404 (-NH), 1622 (C=N), 2835-2939 (C-H aliphatic). (Calcd). Found, for $C_{14}H_{13}N_3O$ (253.29) : C(72.13) H(6.91%) N(15.19)

O(7.32) % Found: C 72.14 ; H 6.96 ; N 15.58 ; O 7.33%.

2.10. Preparation of the complexes

An absolute EtOH solution (10 ml) containing 5 mmol of anthranilic acid plus 5 mmol of suitable metal ions, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$. Was added slowly to another absolute EtOH solution (10 ml) containing 5mmol 2-(1*H*-benzimidazol-2-yl)aniline derivatives. The acidity of the mixture was regulating to (PH~ 8) by addition of a little drops of KOH. Mixture of reaction refluxed for 3h, the solvent vaporized by heating to half of volume and Keep it cooled. The precipitate were filtered and washed with cooled distilled water and re-crystallization with EtOH, isolated complexes was dried at 50 ^{0}C overnight.

3. Results and Discussion

The synthesis of the ligands is illustrative in (Figure 2). The prepared ligands offer satisfactory analysis for the suggested structures, which was specified depends on spectral and elemental analysis [FT-IR , ^{1}H NMR and (C, H, N, O)] data. Several complexes ions Cobalt, Nickel, Copper, Zinc with mix ligands, was prepared by the reaction of 1:1:1 ratio of Metal with primary, secondary ligands in ethanol are represented in (Figure 4).

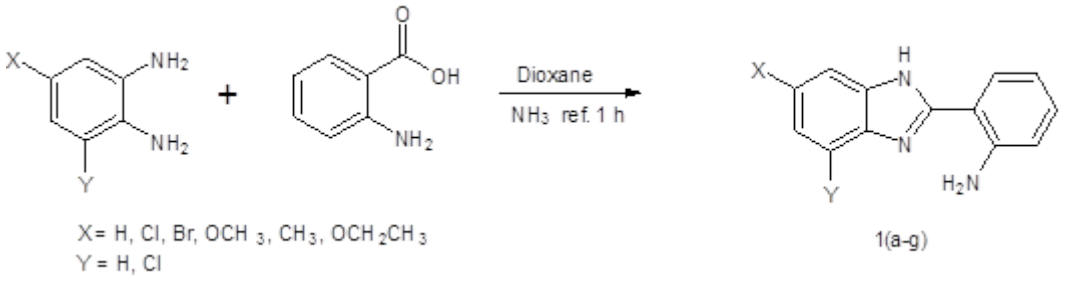


Figure 2: Preparation of ligands.

The suggested mechanism for formation of 2-(1H-benzimidazol-2-yl)aniline derivatives (BIAD) showing in (Figure 3).

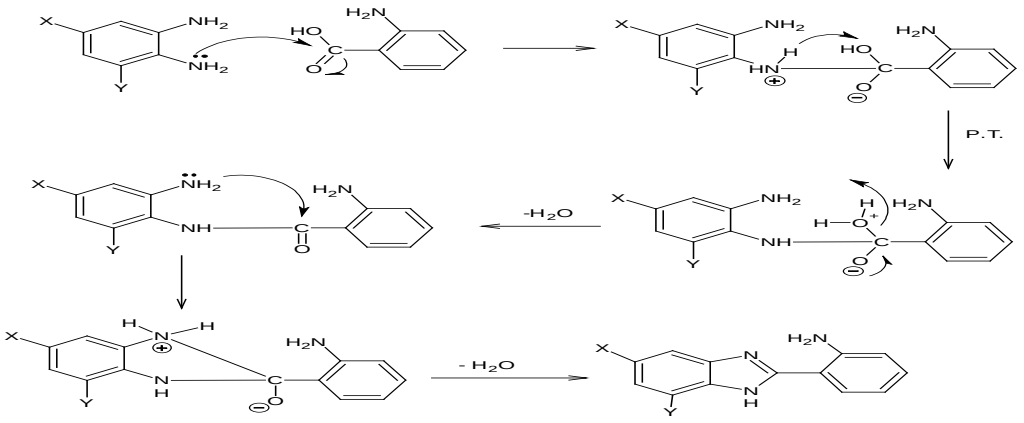


Figure 3: The suggested mechanism for formation of (BIAD).

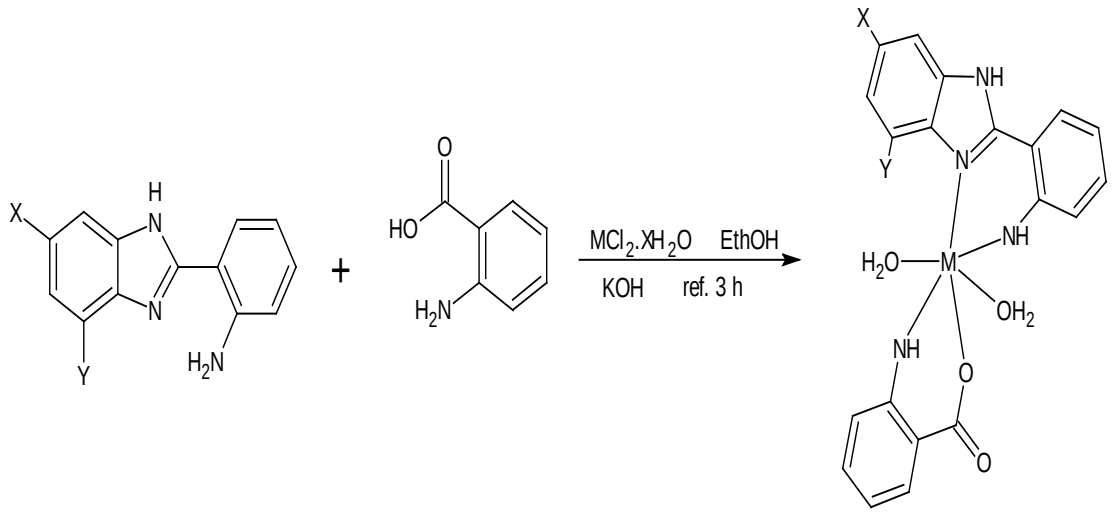


Figure 4: Reaction of (Cu-, Ni-, Zn- and Co-) with primary, secondary ligands.

Complexes are colored solids, non-hygroscopic, stable, excellent yields, insoluble in water, ethanol, partially in methanol and soluble in DMF and DMSO. DMF solvent were applied after appropriate dilution for metal analysis. Elemental analyses (C, H, N, O) and atomic absorption technique were Elements and metal contents of the complexes was measured (Table 3). The elemental analysis (molar conductivity, magnetic moments) data of complexes (Table 2) indicate that all complexes are of the nature electrolyte (1 : 3 electrolyte type) in DMF (10^{-3} M) [21,22].

Table 2: Analytical data and some physical properties of complexes.

number	complexes	Chemical Formula	F.W(g·mol^{-1})	colour	M. Point(°C)	Yield (%)	Meff (B.M.)	Conductivity Cohm^{-1}. cm^2.mol^{-1}
1	[Co(1a)(Ant)(H_2O)$_2$]	$C_{13}H_{12}N_3O_2Co$	438.3	Pale green	178-180	73	3.89	221
2	[Ni(1a)(Ant)(H_2O)$_2$]	$C_{13}H_{12}N_3O_2Ni$	438.08	Gray	>300	79	3.1	213
3	[Cu(1a)(Ant)(H_2O)$_2$]	$C_{13}H_{12}N_3O_2Cu$	442.9	Deep orange	195-197	77	1.9	211
4	[Zn(1a)(Ant)(H_2O)$_2$]	$C_{13}H_{12}N_3O_2Zn$	444.8	yellow	156-159	68	0	232
5	[Co(1b)(Ant)(H_2O)$_2$]	$C_{13}H_{11}ClN_3O_2Co$	472.7	Dark brown	217-220	89	4.1	237
6	[Ni(1b)(Ant)(H_2O)$_2$]	$C_{13}H_{11}ClN_3O_2Ni$	472.5	Pale green	>300	83	3.1	203
7	[Cu(1b)(Ant)(H_2O)$_2$]	$C_{13}H_{11}ClN_3O_2Cu$	477.3	blue	>300	85	1.8	207

8	[Zn(1b)(Ant)(H_2O)$_2$]	$C_{13}H_{11}ClN_3O_2Zn$	479.2	yellow	220 de	73	0	240
9	[Co(1c)(Ant)(H_2O)$_2$]	$C_{13}H_{10}Cl_2N_3O_2Co$	507.2	pale brown	221-223	79	3.9	226
10	[Ni(1c)(Ant)(H_2O)$_2$]	$C_{13}H_{10}Cl_2N_3O_2Ni$	506.9	green	177-180	69	2.88	218
11	[Cu(1c)(Ant)(H_2O)$_2$]	$C_{13}H_{10}Cl_2N_3O_2Cu$	511.8	Violet	233-236	83	1.76	235
12	[Zn(1c)(Ant)(H_2O)$_2$]	$C_{13}H_{10}Cl_2N_3O_2Zn$	513.7	Gray	>300	85	0	231
13	[Co(1d)(Ant)(H_2O)$_2$]	$C_{13}H_{11}BrN_3O_2Co$	517.2	pale brown	187-200	66	4.3	234
14	[Ni(1d)(Ant)(H_2O)$_2$]	$C_{13}H_{11}BrN_3O_2Ni$	517.0	green	213-216	91	3.4	203
15	[Cu(1d)(Ant)(H_2O)$_2$]	$C_{13}H_{11}BrN_3O_2Cu$	521.8	Deep violet	230-233	74	1.9	223
16	[Zn(1d)(Ant)(H_2O)$_2$]	$C_{13}H_{11}BrN_3O_2Zn$	523.7	Gray	214-217	79	0	214
17	[Co(1e)(Ant)(H_2O)$_2$]	$C_{14}H_{14}N_3O_3Co$	468.3	pale brown	>300	85	4.5	235
18	[Ni(1e)(Ant)(H_2O)$_2$]	$C_{14}H_{14}N_3O_3Ni$	468.1	green	>300	71	3.3	225
19	[Cu(1e)(Ant)(H_2O)$_2$]	$C_{14}H_{14}N_3O_3Cu$	478.0	Deep brown	>300	91	1.78	229
20	[Zn(1e)(Ant)(H_2O)$_2$]	$C_{14}H_{14}N_3O_3Zn$	474.8	gray	>300	80	0	231
21	[Co(1f)(Ant)(H_2O)$_2$]	$C_{14}H_{14}N_3O_2Co$	452.3	pale brown	143-146	75	4.7	205
22	[Ni(1f)(Ant)(H_2O)$_2$]	$C_{14}H_{14}N_3O_2Ni$	452.1	yellow	184-188	78	3.4	232
23	[Cu(1f)(Ant)(H_2O)$_2$]	$C_{14}H_{14}N_3O_2Cu$	457.0	Deep violet	122-125	83	2.0	214
24	[Zn(1f)(Ant)(H_2O)$_2$]	$C_{14}H_{14}N_3O_2Zn$	458.8	Gray	200-203	90	0	238
25	[Co(1g)(Ant)(H_2O)$_2$]	$C_{15}H_{16}N_3O_3Co$	482.3	pale brown	>300	82	4.8	236
26	[Ni(1g)(Ant)(H_2O)$_2$]	$C_{15}H_{16}N_3O_3Ni$	482.1	blue	269-272	76	2.87	210
27	[Cu(1g)(Ant)(H_2O)$_2$]	$C_{15}H_{16}N_3O_3Cu$	487.0	Violet	280-283	69	1.9	219
28	[Zn(1g)(Ant)(H_2O)$_2$]	$C_{15}H_{16}N_3O_3Zn$	488.8	Gray	240-242	64	0	207

Elemental analysis exhibit in the (table-3-) show that all mixed-ligand Complexes have (1:1:1) stoichiometry with estimate (Metal: BIAD : Ant.) , all of them have a dark colored amorphous substances.

Table 3: Analytical data of complexes.(M = Co ,Ni, Cu, Zn)

Complexes	% C (Calcd).Found	% H (Calcd).Found	% N (Calcd).Found	%O (Calcd).Found	%M (Calcd).Found
[Co(1a)(Ant)(H_2O)$_2$]	(54.80) 54.78	(4.37) 4.35	(12.78) 12.68	(14.60) 14.68	(13.45) 13.51
[Ni(1a)(Ant)(H_2O)$_2$]	(54.83) 54.81	(4.37) 4.35	(12.79) 12.75	(14.61) 14.59	(13.40) 13.44
[Cu(1a)(Ant)(H_2O)$_2$]	(54.23) 54.78	(4.32) 4.30	(12.65) 12.63	(14.45) 14.41	(14.35) 14.39
[Zn(1a)(Ant)(H_2O)$_2$]	(54.01) 54.04	(4.31) 4.29	(12.60) 12.65	(14.39) 14.36	(14.71) 14.84
[Co(1b)(Ant)(H_2O)$_2$]	(50.81) 50.83	(3.84) 3.81	(11.85) 11.82	(13.54) 13.52	(12.47) 12.32
[Ni(1b)(Ant)(H_2O)$_2$]	(50.84) 50.82	(3.84) 3.84	(11.86) 11.84	(13.54) 13.51	(12.42) 12.37
[Cu(1b)(Ant)(H_2O)$_2$]	(50.32) 50.35	(3.80) 3.78	(11.74) 11.71	(13.41) 13.38	(13.31) 13.43
[Zn(1b)(Ant)(H_2O)$_2$]	(50.12) 50.09	(3.79) 3.76	(11.69) 11.65	(13.35)13.32	(13.65) 13.75
[Co(1c)(Ant)(H_2O)$_2$]	(47.36) 47.34	(3.38) 3.36	(11.05) 11.11	(12.62) 12.58	(11.62) 11.58
[Ni(1c)(Ant)(H_2O)$_2$]	(47.38) 47.36	(3.38) 3.35	(11.05) 11.12	(12.62)12.59	(11.58) 11.56
[Cu(1c)(Ant)(H_2O)$_2$]	(46.93) 46.91	(3.35) 3.33	(10.95) 10.93	(12.50) 12.47	(12.42) 12.39
[Zn(1c)(Ant)(H_2O)$_2$]	(46.76) 46.74	(3.34) 3.32	(10.91) 10.88	(12.46) 12.43	(12.73) 12.70
[Co(1d)(Ant)(H_2O)$_2$]	(46.44) 46.41	(3.51) 3.49	(10.83) 10.80	(12.37) 12.35	(11.39) 11.36
[Ni(1d)(Ant)(H_2O)$_2$]	(46.46) 46.44	(3.51) 3.47	(10.84) 10.87	(12.83) 12.80	(11.35) 11.32
[Cu(1d)(Ant)(H_2O)$_2$]	(44.85) 44.89	(3.37) 3.34	(11.01) 11.05	(12.58) 12.56	(12.49) 12.47
[Zn(1d)(Ant)(H_2O)$_2$]	(45.87) 45.93	(3.46) 3.44	(10.70) 10.68	(12.22) 12.20	(12.49) 12.47
[Co(1e)(Ant)(H_2O)$_2$]	(53.85) 53.82	(4.52) 4.49	(11.96) 11.94	(17.08) 17.11	(12.58) 12.55
[Ni(1e)(Ant)(H_2O)$_2$]	(53.88) 53.82	(4.52) 4.49	(11.97) 11.95	(17.09) 17.06	(12.54) 12.51
[Cu(1e)(Ant)(H_2O)$_2$]	(53.33) 53.42	(4.48) 4.47	(11.85) 11.82	(16.91) 16.95	(13.44) 13.41
[Zn(1e)(Ant)(H_2O)$_2$]	(53.12) 53.18	(4.46) 4.43	(11.80) 11.76	(16.85) 16.89	(13.78) 13.75
[Co(1f)(Ant)(H_2O)$_2$]	(55.76) 55.83	(4.68) 4.66	(12.39) 12.36	(14.15) 14.12	(13.03) 13.01
[Ni(1f)(Ant)(H_2O)$_2$]	(55.79) 55.85	(4.68) 4.63	(12.39) 12.37	(14.16) 14.13	(12.98) 12.95
[Cu(1f)(Ant)(H_2O)$_2$]	(55.20) 55.24	(4.63) 4.60	(12.26) 12.24	(14.01) 14.06	(13.91) 13.88
[Zn(1f)(Ant)(H_2O)$_2$]	(54.97) 54.93	(4.61) 4.57	(12.21) 12.18	(13.95) 13.91	(14.26) 14.23
[Co(1g)(Ant)(H_2O)$_2$]	(54.78) 54.74	(4.81) 4.78	(11.61) 11.59	(16.58) 16.55	(12.22) 12.19
[Ni(1g)(Ant)(H_2O)$_2$]	(54.81) 54.77	(4.81) 4.77	(11.62) 11.58	(16.59) 16.57	(12.17) 12.15
[Cu(1g)(Ant)(H_2O)$_2$]	(54.26) 54.23	(4.76) 4.73	(11.50) 11.57	(16.43) 16.41	(13.05) 13.02
[Zn(1g)(Ant)(H_2O)$_2$]	(54.05) 54.10	(4.74) 4.71	(11.46) 11.43	(16.36) 16.34	(13.38) 13.35

3.1. Infrared spectra

The FT-IR of ligands show perfect value of peaks which conform the structure, the spectra of complexes Showed disappear some of active group peaks and appear the new peaks (Table 4). In complexes spectra υ(-NH_2) frequency of sharp absorption bands (~3415-3422 cm^{-1}) of 2-(1*H*-benzimidazol-2-yl)aniline derivatives (BIAD) disappearance , also disappear the band at (3592 cm^{-1}),(3394-3542 cm^{-1} symmetric and asymmetric) corresponding to (O–H), (NH_2) stretching respectively in anthranilic acid [23], that conclusive evidence of coordinate metal ions both by nitrogen of NH_2 group (in BIAD, Ant.) and oxygen atoms of the carboxylic group. This was also confirmed by outcrop of a new band at (~420 , ~535 cm^{-1}) due to the υ(M-O, M-N) respectively (Table 4). The clear, new interesting bands can be observed at (~3745 cm^{-1}) which related to H_2O molecules [24,25] , and that good evidence of Participate the H_2O molecules in inner coordination sphere of complexes. The bands shifts of active group (C=O) in complexes can be observed in comparison with free anthranilic acid bands.

Table 4: FT-IR spectral data in cm^{-1} to the complexes.

complexes	υ O-H	υ N-H_2 Ant.	υ N-H_2 BIAD	υ N-H BIAD	υ (C-H) Aliph	υ Ar-Cl	υ Ar-Br	υ C=O Ant.	υ H_2O	υ (M-N)	υ (M-O)
[Co(1a)(Ant)(H_2O)$_2$]	----	---	---	3404	---	---	---	1712	3732	521	437
[Ni(1a)(Ant)(H_2O)$_2$]	---	---	---	3411	---	---	---	1710	3711	523	430
[Cu(1a)(Ant)(H_2O)$_2$]	---	---	---	3409	---	---	---	1717	3749	521	452
[Zn(1a)(Ant)(H_2O)$_2$]	---	---	---	3403	---	---	---	1724	3718	554	412
[Co(1b)(Ant)(H_2O)$_2$]	---	---	---	3389	---	**1045**	---	1694	3743	513	423
[Ni(1b)(Ant)(H_2O)$_2$]	---	---	---	3393	---	---	---	1697	3708	523	411
[Cu(1b)(Ant)(H_2O)$_2$]	---	---	---	3378	---	---	---	1685	3774	544	404
[Zn(1b)(Ant)(H_2O)$_2$]	---	---	---	3421	---	---	---	1701	3714	560	409
[Co(1c)(Ant)(H_2O)$_2$]	---	---	---	3417	---	**1094**	---	1705	3775	545	423
[Ni(1c)(Ant)(H_2O)$_2$]	---	---	---	3411	---	---	---	1707	3753	543	452
[Cu(1c)(Ant)(H_2O)$_2$]	---	---	---	3407	---	---	---	1715	3747	526	428
[Zn(1c)(Ant)(H_2O)$_2$]	---	---	---	3414	---	---	---	1711	3742	513	416
[Co(1d)(Ant)(H_2O)$_2$]	---	---	---	3406	---	---	**105**	1709	3735	527	411

							5				
[Ni(1d)(Ant)(H_2O)$_2$]	---	---	---	3402	---	---	---	1718	3738	543	458
[Cu(1d)(Ant)(H_2O)$_2$]	---	---	---	3397	---	---	---	1712	3726	536	437
[Zn(1d)(Ant)(H_2O)$_2$]	---	---	---	3393	---	---	---	1710	3731	524	417
[Co(1e)(Ant)(H_2O)$_2$]	---	---	---	3410	**2861-2987**	---	---	1713	3718	513	435
[Ni(1e)(Ant)(H_2O)$_2$]	---	---	---	3413	---	---	---	1709	3720	540	418
[Cu(1e)(Ant)(H_2O)$_2$]	---	---	---	3396	---	---	---	1707	3729	544	454
[Zn(1e)(Ant)(H_2O)$_2$]	---	---	---	3391	---	---	---	1716	3737	550	436
[Co(1f)(Ant)(H_2O)$_2$]	---	---	---	3418	**2845-2989**	---	---	1712	3742	547	412
[Ni(1f)(Ant)(H_2O)$_2$]	---	---	---	3405	---	---	---	1711	3740	551	445
[Cu(1f)(Ant)(H_2O)$_2$]	---	--	---	3412	---	---	---	1709	3710	537	426
[Zn(1f)(Ant)(H_2O)$_2$]	---	---	---	3406	---	---	---	1702	3716	548	415
[Co(1g)(Ant)(H_2O)$_2$]	---	---	---	3409	**2821-2976**	---	---	1716	3726	536	421
[Ni(1g)(Ant)(H_2O)$_2$]	---	---	---	3417	---	---	---	1713	3729	529	431
[Cu(1g)(Ant)(H_2O)$_2$]	---	---	---	3399	---	---	---	1709	3716	556	416
[Zn(1g)(Ant)(H_2O)$_2$]	---	---	---	3392	---	---	---	1711	3715	531	440

3.2. ^{1}H NMR spectra of the compounds

^{1}H NMR spectra data of the complexes was gained at d_6 - DMSO in (R.T.) utilize TMS as an internal standard (Table 5).

Chemical shift of the NH_2 protons in the ligands (~5.7 ppm for BIAD),(8.4 ppm for Ant.) was not noted in all the complexes. This conforms the bind of nitrogen and oxygen to the metal ions (N-M, O-M). The similarly result was proven by the FT-IR spectra.

The singlet signal at δ 4.2–4.1 ppm appear due to the H_2O atoms from the coordinated water molecule. All other absorption bands for the aromatic, aliphatic and (NH benzimidazole) protons in the ligands are in the same chemical shift and not affected by coordination.

Table 5: ^{1}H NMR spectra of the complexes in d_6-DMSO (δ ppm)**.**

complexes	OH	NH_2	New NH	OH_2
[Co(1a)(Ant)$(H_2O)_2$]	---	---	4.3	4.2
[Ni(1a)(Ant)$(H_2O)_2$]	---	---	4.3	4.2
[Cu(1a)(Ant)$(H_2O)_2$]	---	---	4.3	4.1
[Zn(1a)(Ant)$(H_2O)_2$]	---	---	4.3	4.2
[Co(1b)(Ant)$(H_2O)_2$]	---	---	4.3	4.1
[Ni(1b)(Ant)$(H_2O)_2$]	---	---	4.3	4.1
[Cu(1b)(Ant)$(H_2O)_2$]	---	---	4.3	4.2
[Zn(1b)(Ant)$(H_2O)_2$]	---	---	4.3	4.2
[Co(1c)(Ant)$(H_2O)_2$]	---	---	4.4	4.1
[Ni(1c)(Ant)$(H_2O)_2$]	---	---	4.4	4.2
[Cu(1c)(Ant)$(H_2O)_2$]	---	---	4.4	4.2
[Zn(1c)(Ant)$(H_2O)_2$]	---	---	4.4	4.1
[Co(1d)(Ant)$(H_2O)_2$]	---	---	4.4	4.2
[Ni(1d)(Ant)$(H_2O)_2$]	---	---	4.4	4.2
[Cu(1d)(Ant)$(H_2O)_2$]	---	---	4.4	4.2
[Zn(1d)(Ant)$(H_2O)_2$]	---	---	4.4	4.2
[Co(1e)(Ant)$(H_2O)_2$]	---	---	4.4	4.1
[Ni(1e)(Ant)$(H_2O)_2$]	---	---	4.4	4.1
[Cu(1e)(Ant)$(H_2O)_2$]	---	---	4.4	4.2
[Zn(1e)(Ant)$(H_2O)_2$]	---	---	4.4	4.2
[Co(1f)(Ant)$(H_2O)_2$]	---	---	4.4	4.2
[Ni(1f)(Ant)$(H_2O)_2$]	---	---	4.4	41
[Cu(1f)(Ant)$(H_2O)_2$]	---	---	4.4	41
[Zn(1f)(Ant)$(H_2O)_2$]	---	---	4.4	4.1
[Co(1g)(Ant)$(H_2O)_2$]	---	---	4.4	4.2
[Ni(1g)(Ant)$(H_2O)_2$]	---	---	4.4	4.1
[Cu(1g)(Ant)$(H_2O)_2$]	---	---	4.4	4.2
[Zn(1g)(Ant)$(H_2O)_2$]	---	---	4.4	4.2

4. Conclusion

In summary, we have synthesized and characterized ligands of (BIAD), prepared in this work through condensation of anthranilic acid and *o*-phenylenediamine derivatives in suitable solvent (dioxin). Twenty-eight complexes of mixed ligand with (Co^{II} ,Ni^{II}, Cu^{II}, Zn^{II}) ions were prepared and characterized through {FT-IR,

^{1}H NMR, (C, H, N, O) analysis, atomic absorption, Magnetic susceptibilities, Molar conductance}. Data of all Previous Techniques support octahedral geometry for all metal complexes. Depends on the spectral and physical data of ligands and complexes which discussed previously, one can suppose that the metal ions are bind to the ligands through the carboxylic oxygen and amino nitrogen as clarify in Figure 1.

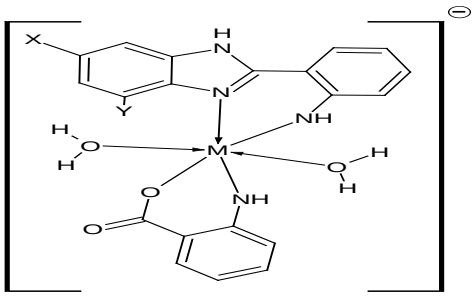


Figure 1: The suggested geometry of complexes. M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}.

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