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Co(II) AND Ni(II) COMPLEXES WITH BIS(4-((E)-(4,5-DIPHENYL-1H-IMIDAZOL-2-YL)DIAZENYL)PHENYL)METHANE: SYNTHESIS, CHARACTERIZATION AND ANTI-CORROSION EFFECT INVESTIGATION

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ABSTRACT. Bright coloured Co (II) and Ni (II) complexes of an azo ligand were synthesized. This ligand was previously synthesized from the coupling reaction between 4,5-diphenyl imidazole and 4,4-diaminodiphenylmethane in 1:2 molar ratio (4,4-diaminodiphenylmethane and 4,5-diphenyl imidazole). The synthesis process of the complexes involved the reflux reaction between the azo ligand with both metal salts. The synthesized complexes were characterized by FTIR, UV.-Visible, molar conductivity and atomic absorption. From the obtained characteristic data of the FTIR spectra, the coordination between the two metals and the azo ligand occurs by the coordination with the nitrogen atom of the azo group and one of the nitrogen atoms in the imidazole both rings. The molar conductivity test confirm the non- electrolytic nature of both complexes, while the atomic absorption agrees with the expected complexes formula. Therefore, the octahedral structure for the two complexes is suggested. The anti-corrosion activity of the synthesized compounds were investigated under two temperatures (298 and 308 K) with 0.03 gm of each compound was tested. According to the results cobalt (II) complex shows a better anti-corrosion activity (93%) in comparison with the ligand and nickel (II) complex.

KEY WORDS: Cobalt(II) and nickel(II) azo complexes, Imidazole derivative, Anti-corrosion effect

INTRODUCTION

Both cobalt and nickel with their compounds are considered as important and more studied ones. Thanks to their attractive features which have led to use them in various fields. Cobalt discovery is back to the eightieth century [1]. Both metals can be found in the environment, namely in air, water and soil [2, 3]. Cobalt also can be found in human organs in trace amounts as these amounts are crucial for human life. It is also considered as important element for its formation of vitamin B12 which is important for the nervous system work and also its deficiency leads to anemia [4]. Cobalt acts as a coenzyme and acts as a building block for some amino acids. Nickel also involved enzymes and it is important for some live species as nutrition source [2]. In addition to these biological importance, cobalt and nickel have been used in industry as catalysts, in alloys formation, batteries production and as anti- corrosion inhibitors [2, 5-7].

In addition to these applications, in academic research both metals can form with electron rich molecules special compounds which are called complexes [8, 9]. In these complexes both cobalt and nickel can be found in various oxidation states and form bonds with these electron rich molecules that have special donating atoms, such as N, O and S [10]. Some of such molecules with these atoms are called hetero- molecules [11, 12]. An example of them is imidazole which is related to the azole compounds with their five atoms in their chemical structure. These five atoms form the imidazole aromatic ring with the presence of the interesting non adjacent two nitrogen atoms [13]. Therefore imidazole can be found in the two following forms depending on the position of the hydrogen atom on the two nitrogen atoms [14, 15].

Occasionally imidazole bonds with metal ions as a free ligand or even as a part of a whole ligand molecule. An example of the latest ligands is azo dyes containing imidazole ring. These dyes are considered as the most important and interesting ligands due to the presence of azo group [16]. This group consists of also two nitrogen atoms linked directly together (-N=N-) [17-19]. As

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*Corresponding author. E-mail: wsci.suaad.taha@uobabylon.edu.iq a result, the formed complex involves a linkage between the metal ion with the azo group, the imidazole nitrogen atom and even other available groups or atoms suitable for coordination in the ligand chemical structure to form the stable chelate ring [20-22]. The resulted complex containing imidazole and azo group as a coordinating ligand is well known for its significant biological and industrial importance [23, 24].

In this paper cobalt(II) and nickel(II) azo complexes with imidazole containing ligand were synthesized and their activity against corrosion was investigated.

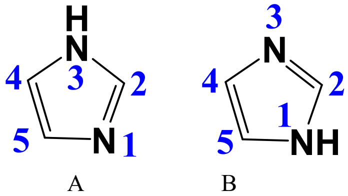


Figure 1. Imidazole two possible forms.

EXPERIMENTAL

Materials

The supplier of diphenylimidazole and 4,4-diaminodiphenylmethane was Macklin. Co^{2+}, Ni^{2+} chlorides and ethanol were purchased from Merck, CDH and Scharlau, respectively.

Instrumentations

The infrared spectra were measured using (FTIR spectrophotometer – 8400S) from Shimadzu. The UV-Visible spectrophotometer (CECIT CE 7200, 7000 series) from Aquaris was used to investigate the electronic transitions. Metals percentage in complexes was detected using Nova 350 spectrophotometer. Cond 722 apparatus from WTW SERIES was used to measure the conductivity. Melting points were measured using melting point / SMP30 Stuart apparatus.

Procedures

Synthesis of azo ligand (A). The ligand synthesis was described previously in the literature [25].

Synthesis of Co(II) and Ni(II) complexes. The synthesis of nickel(II) and cobalt(II) complexes included the reflux reaction between the azo ligand (0.4 g, 0.6053 mmol) with Co(II) and Ni(II) hexahydrate chlorides (0.144 g, 0.6053 mmol) which were dissolved in ethanol: water mixture (40: 5ml). The reaction mixture was refluxed for one hour. Red and reddish brown precipitates were formed of Ni(II) and Co(II) complexes, respectively. The precipitates were filtered and washed with water and ethanol.

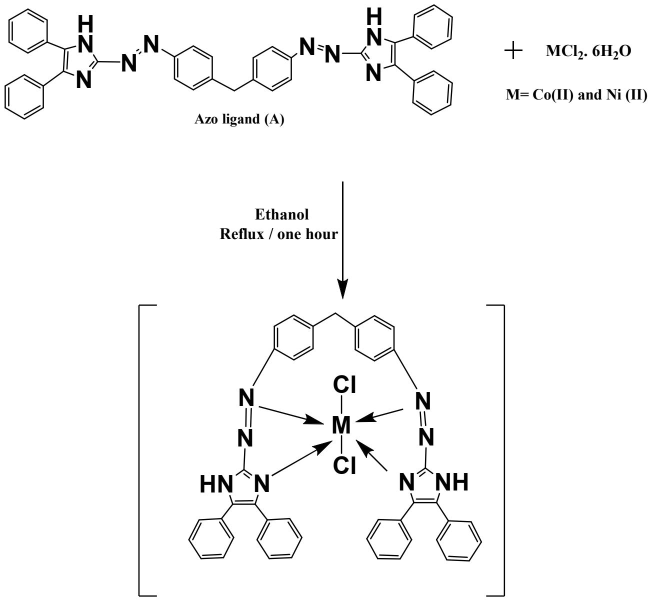
Anti- corrosion study of (A) and metal complexes

This study was carried out at the University of Baghdad-College of Science using the procedures in the literature [26-28]. All tests were carried out at 298 K and 308 K by using a water bath and 0.03 g of the synthesized compounds. The tested samples were inserted in the corrosion cell in which the diameter of the exposed surface to the solution was (16.55 cm^2).

RESULTS AND DISCUSSION

Ligand and metal complexes synthesis

The synthesis of both metal complexes were carried out by mixing the previously prepared azo ligand with the two mentioned metal chlorides. This mixing was enhanced by the reflux reaction between the two components in (1:1) ligand:metal molar ratio. The synthesis of the complexes is shown in Schemes 1, while Table 1 gives some properties of both complexes.



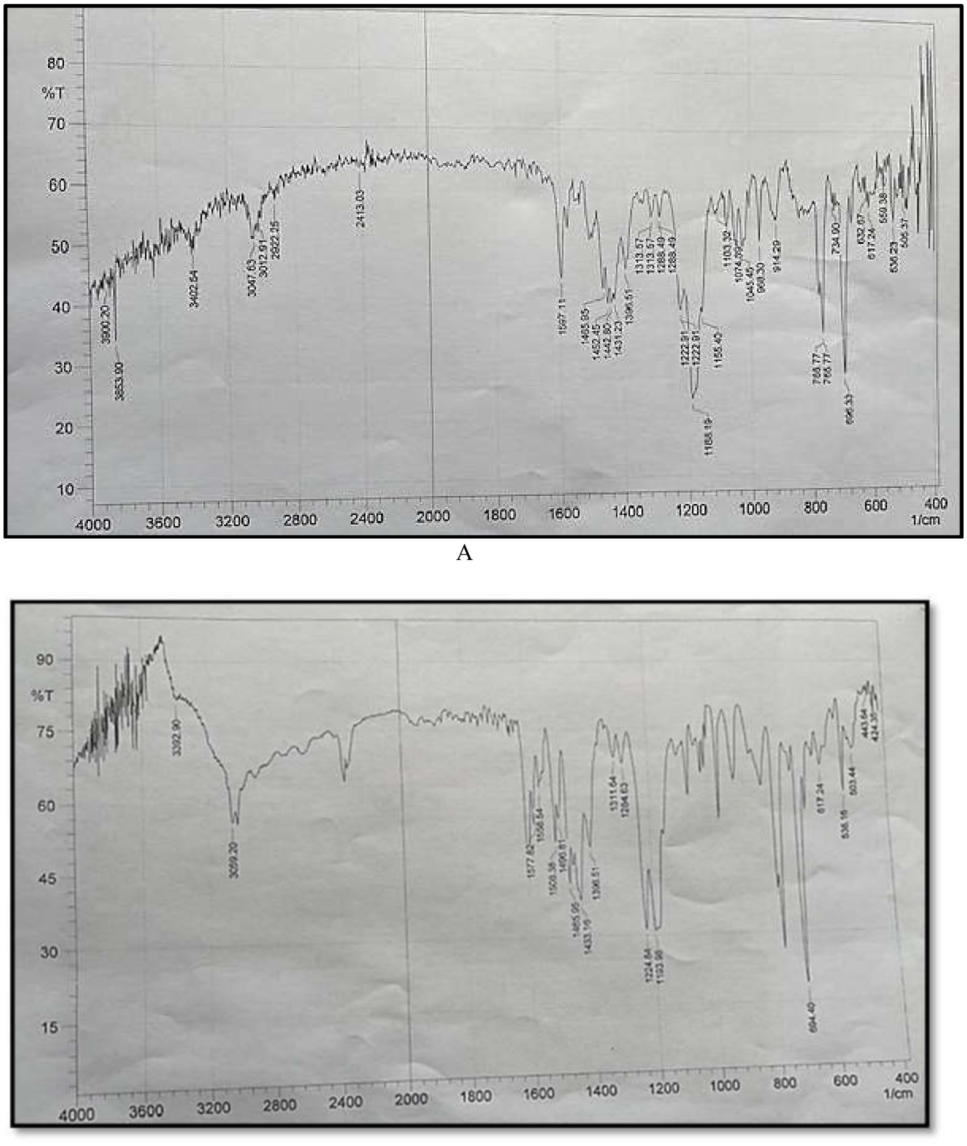
Scheme 1. Co(II) and Ni(II) azo complexes.

Table 1. Properties of the divalent metal ion complexes.

Complex	Colour	m.p. °C	M.wt.	Yield %
$[Co(A)Cl_2]$	Reddish brown	213-215	790.62	63
$[Ni (A)Cl_2]$	Red	169-171	790.38	62

Infrared spectra

The infrared spectra of both complexes are shown in Figure 2. Both spectra give the important and the characteristic bands in the complexes chemical structure which confirm the complexes formation. The mentioned before bands in the ligand spectrum namely, the –NH–, (C=N) in the imidazole ring and the azo group appear at 3394, 1597 and 1435 cm^{-1}, respectively. In both complexes, these bands are shifted or changed in their intensities which suggest the complexes formation. For example, the –NH– group in the imidazole ring is slightly shifted to 3402 and 3392 cm^{-1} in Co(II) and Ni(II) complexes respectively. While the (C=N) of the imidazole is changed in its intensity and that suggests the coordination with the metals by this group as this stimulated from the previously published articles. Finally, the azo group which appears at 1435 cm^{-1} in the free ligand was shifted to 1433 and 1442 cm^{-1} in Co(II) and Ni(II) complexes, respectively, which suggests the coordination between the metal and the ligand azo group. Other new bands at 589 and 569 cm^{-1} refer to the formation of M-N bond type in Co(II) and Ni(II) complexes, respectively. Table 2 gives a summary of FT-IR data of the complexes.



A

B

Figure 2. FTIR spectra of (A): Co(II) and (B): Ni (II) complexes.

Table 2. FT-IR data in cm^{-1} for both complexes.

Compound	–NH–	(C-H) (aromatic)	(C-H)(aliphatic)	(N=N)	(C=N)	(M-N)
$[Co(A)Cl_2]$	3402	3051	2922	1442	1597	589
$[Ni(A)Cl_2]$	3392	3066	2910	1433	1597	569

Electronic spectra

The UV-Vis. Spectra of of Co(II) and Ni(II) complexes are recorded in ethanol and shown in Figure 3. As mentioned in the previous paper the ligand has two peaks in the visible region appears at 407 and 448 nm, respectively [25]. These two peaks are shifted to higher wavelengths as given in Table 3 and they are related to charge transfer transition. This shift indicates the complexes formation.

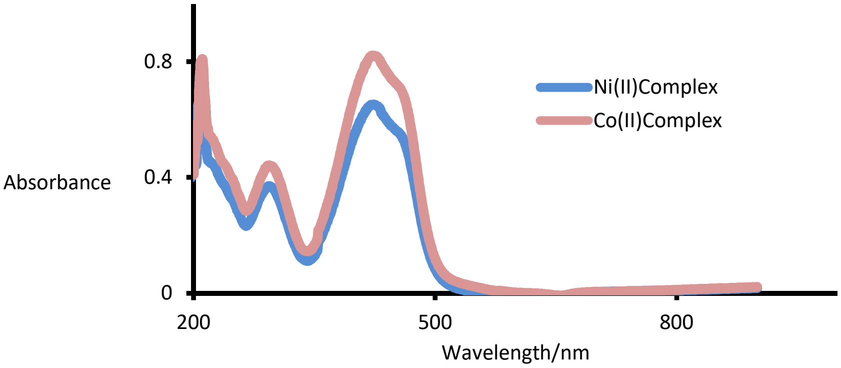


Figure 3. UV-Visible spectra of the complexes.

Table 3. Suggested electronic transitions for the complexes.

Compound	λmax	Type of transition
$[Co(A)Cl_2]$	287 416 453	MLCT
$[Ni(A)Cl_2]$	277 413 471	MLCT

Molar conductivity measurements and metal content

The concentration of the studied complexes was 10^{-3} M when their molar conductivity was measured. Table 4. Gives the conductivity data of them. These data showed that both complexes were non-electrolyte and that gives explanation of the presence of two chloride ions inside the coordination sphere [29]. On the other hand, the atomic absorption data confirm the suggested complexes octahedral structure, where the coordination between the metals with one ligand molecule and the two chloride ions.

Table 4. Molar conductivity measurements, metal content and the proposed complexes structure.

Complex	Molar conductivity ($Ohm^{-1}.mol^{-1}.cm^{-1}$)	Metal content%		Structure for the complex
		(Theoretical value)	(Practical value)	
[$Co(A)Cl_2$]	1.6	7.45	8.792	Octahedral
[$Ni(A)Cl_2$]	2.8	7.43	7.937	Octahedral

Anti-corrosion effect study

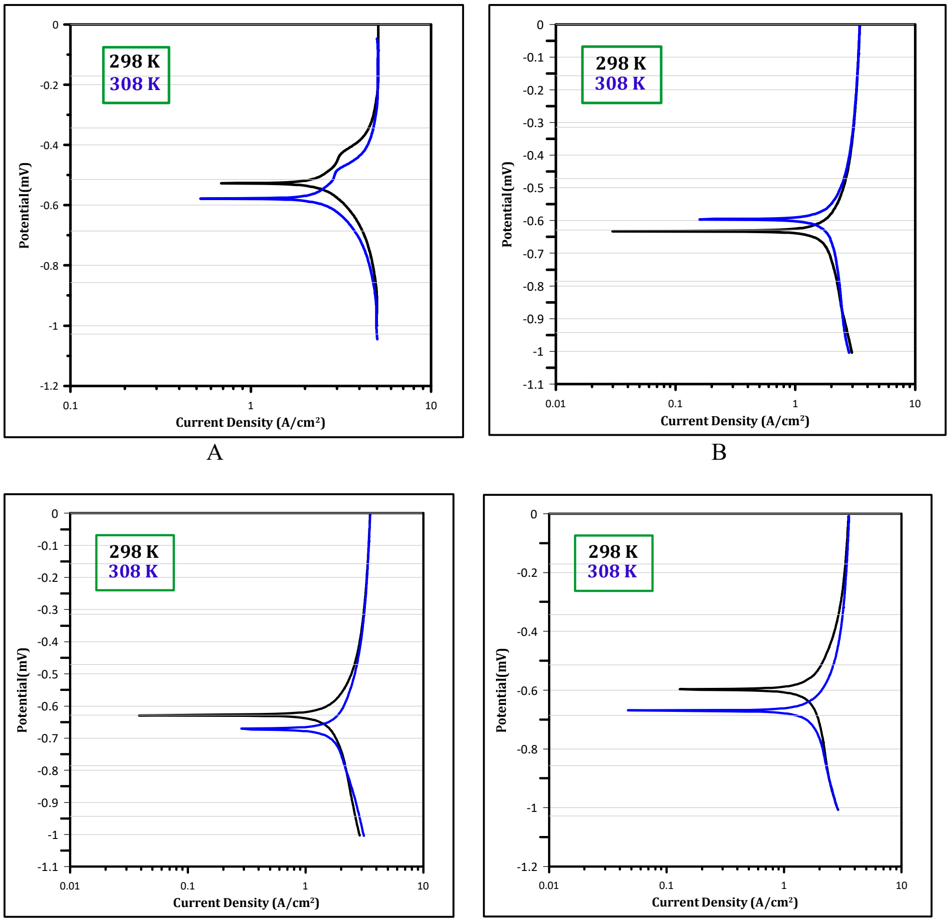
A carbon steel with components were mentioned in the literature was used as a working electrode where its corrosion was studied [26]. The ligand and the two complexes were tested as corrosion inhibitors with the weight (0.03 g) and at two temperatures (298 K and 308 K). The studied parameters values are given in Table 5. as they involved the corrosion current density (Icorr) (μA) and corrosion potential (Ecorr) (V) were obtained by the extrapolation of the cathodic and anodic Tafel constants (V/decade) under the experiments conditions which include the absence and in the presence of the studied compounds in hydrochloric acid (0.1 M) solution. The resulting data are potential Ecorr (mV), corrosion current density icorr (A/cm^2), cathodic (βc) and anodic (βa) Tafel slopes (mV/Dec) were calculated and finally the protection efficiency IE% was calculated from the equation showed below [30]:

$$\%\mathrm{IE} = \frac{\mathbf{(icorr)o-(icorr)}}{\mathbf{(icorr)o}} * 100 \tag{1}$$

where $(icorr)_0$ and (icorr) are the corrosion current density with the non-availability and the availability of the inhibitors respectively. The concluded results suggest that the synthesized compounds showed a good protection ability against corrosion. In detail, both complexes showed a better anti-corrosion activity at the lowest temperature 298 K in comparison with the ligand. However, cobalt(II) complex gave at the lowest temperature 298 K the higher corrosion inhibition (93%), while nickel(II) is slightly less active with (92%) protection efficiency. Table 5 also gives the values of the protection efficiency for the azo ligand and both complexes. This high corrosion inhibition can be explained by the adsorption process. An adsorption of the metal complex occurs on the carbon steel surface and that creates a layer on the latest and finally prevents its corrosion. Also, can be explained by a coordination bond can be formed when the electrons transferred from the inhibitor to d-orbitals of iron presents in the carbon steel [30-33]. In addition, molecules with high formula weight give the higher corrosion inhibition activity [34].

Table 5. Corrosion parameters for the synthesized compounds on the carbon steel in HCl solution.

Comp.	Temp. K	Ecorr.	Icorr.	Icorr./r	Resis.	Anodic β	Cathodic β	Corr. rate	IE%
Blank	298	-0.527	392.1	7.842E-4	65.32	0.112	0.125	3.849	-
	308	-0.521	412.4	8.248E-4	64.69	0.112	0.136	4.048	-
Azo ligand	298	-0.635	48.98	7.447E-5	1672	0.221	0.408	0.366	88
	308	-0.590	51.65	1.033E-4	1418	0.231	0.624	0.507	87
Co(II) complex	298	-0.630	28.43	5.685E-5	1931	0.195	0.360	0.279	93
	308	-0.690	31.03	6.207E-5	1642	0.237	0.232	0.305	92
Ni(II) complex	298	-0.596	31.56	6.313E-5	2144	0.230	0.481	0.310	92
	308	-0.684	35.15	7.030E-5	1758	0.227	0.381	0.345	91



A B

C D

Figure 4. Polarization curves for corrosion of the blank (HCl solution) (A), with the azo ligand (B), with Co(II) complex (C) and with Ni(II) complex (D).

CONCLUSION

The previously synthesized ligand was used to form two complexes with divalent nickel and cobalt ions. These synthesized compounds were characterized by different techniques. By the results of them the shape of the complexes is suggested to be octahedral. The anti-corrosion activity of the azo ligand, Co(II) and Ni(II) complexes were examined. The results show the highest anti-corrosion activity of Co(II) complex (93%) at 298 K in comparison with the ligand and Ni(II) complex.

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