Preparation, Characterization of new nitro-chalcone azo ligands and their divalent ionic complexes

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Abstract. In this study two of nitro-chalcone azo ligands were synthesized via the reaction of the diazonium salt of amino p-nitro chalcone (pNAC) with the coupling components (4,5-diphenylimidazole & 2-naphthol) respectively. The new ligands were characterized with many identificational tools such (H1NMR, FTIR and UV-Visible) spectroscopies, in addition to (CHNO)analysis for ensurance of the preparation of these ligands. A UV-Visible study for the aqueous mixtures of three divalent metal ions (Co, Ni and Cu) were perfomed to determination of the (λmax) of their colored mixtures, also to confirm the solid complexes structures via the determination of the suitable mole ratio (M:L), that all complexes mole ratios were (1:2, M:L). The solid complexes were synthesized and characterized by the obvious techniques, indeed, to the complementary techniques such (electrical conductivity, magnetic susceptibility) for determination of the complex formula and suggested their geometries, from the whole results, octahedral geometry can concluded for nitro chalcone azo imidazole complexes with the observation of the ionic characteristic of its, while the second ligand complexes differ from the trahedral for (Co & Cu) complexes and square planer for nickel complex.

Keywords: azo compound, chalcones, azo chalcone, complexes.

Introduction

Azo compounds with the formula (R-N=N-R), where R group may be alphaltic[1,2] (rare) or aromatic [3](more abundant) one of the important organic compounds that entered in textile industry[4] and some of medical prodrugs[5] as well as their ability for coordinating with a huge number of ions and sensitive to a trace amounts of them i.e. they can utilize as (organic reagents).[6]

On the other hand, chalcones (Cleasen-Schmedit condensation) of the acetophenone derivatives and benzaldehyde derivatives (mostly in basic media)[7], give (α, β – unsaturated carbonyl compounds) that utilized widely in the organic synthesis of many many derivatives such (isoxazoline, pyrazoline)[8] via ring closing of chalcones,indeed to other compounds.

Chalcones and their derivatives play an important role in medicine and pharmacy, that their active groups have a vital activity that acts as (antiviral[9], anti inflammatory[10], antimicrobial[11], Antioxidants[12], antineoplastic toxic[13], hypoglycemic[14], antiplatelet [15], Immunosuppressive[16], indeed to others).
Few literatures give in their account the preparation of azo-chalcone compounds[17,18] from the preparation of the azo first, then chalcone, while others prepare the chalcon derivatives first then coupling the azo compound [19-21].

In this study, an attempt to prepare new ligand that contain two important functional groups, such an azo (N=N) and the chalcone moiety, that may enhanced together the activity of the molecules, especially when they substituted with a good active group such a nitro group[22].

**Ligands preparation:-**

**Amino chalcone (pNAC)** was prepared first according to[23]; an eqimolar amount (p-aminoacetophenone ,0.01mole & p-nitrobenzaldehyde ,0.01mole) in a 50 ml absolute ethanol with stirring at 5C, then 3M KOH solution was added drop by drop with stirring and cooling till thickeness, the container kept in refrigrater for tonight and it decanted in cooled ice bath with aciditfy in a dilute HCl, the new chalcone was filtered, washed by DDW, dried and recrystallized in a hot ethanol, then m.p and the yield was determined.

**Azo ligands preparation.** New azo compounds were prepared according to shibata[24] by coupling the diazonium salt of the amino chalcone (previously prepared), with two coupling component (4,5-diphenyl imidazole & 2- Naphthol), 5mmole of (pNAC) was dissolved in a (8ml conc.HCl + 15 ml DW) solution and cooling in the cold ice bath, an eqi-molar solution of NaNO₂ slowly added in the 0C with stirring for 10 min for diazoinum salt formation. Coupling component was prepared by the solvation of 5mmole of each component, in a basic alcoholic solution of 10% NaOH, the addition of the diazoinum salt to the coupling solutions must be in small batches with stirring at 0C. Red colored solution was developed i.e the azo being formed, to complete the precipitation, solutions must be neutralized, the precipitants were filtered, washed twice with DDW to remove the trace of salts formed within reaction, dried and recrystallized with hot ethanol, then yield calculated and the melting point determined.

**Solid complexes preparation.** Solid complexes of three metallic ions (CoII, Ni II and Cu II) were prepared by refluxing them with an agreed amount of the new ligands (pNACAI & pNACAN), as assumed in (M:L) ratio method, that 1 mmole of the ligands solvated in 25ml of ethanol mixed with 10 ml of alcoholic Soln. 0.5 mmole of the selected ion chlorides refluxed for 0.5 hr. the whole solution reduced in boiling water bath then transferred them to a crushed ice bath to develop the colored precipitant of these complexes, they were filtered, washed, recrystalized and the yields & m.p’s were recorded.
Azo ligands preparation sketch

Table 1 - Some physical properties of the ligands and their complexes.

| Compound | MWt. gm/mole | Color     | Yield | m.p C | Elementry Analysis |
|----------|--------------|-----------|-------|-------|-------------------|
| pNAC     | 268.2        | Yellow    | 78%   | 121-123 | C% Found Cal( ) | H% Found Cal( ) | N% Found Cal( ) | M% Found Cal( ) |
| pNACAI   | 499.5        | Red-orange| 73%   | 189-191 | (67.16) | (4.51) | (10.44) | 6.08 |
| Co(pNACAI)₂(H₂O)₂Cl₂ | 1164.9 | Red-brown | 77%  | 211-213 | (61.92) | (3.90) | (12.03) | (5.06) |
| Ni(pNACAI)₂(H₂O)₂Cl₂ | 1169.5 | Brown  | 70%   | 244-247 | (61.93) | (3.90) | (12.04) | (5.04) |
| Cu(pNACAI)₂(H₂O)₂Cl₂ | 1164.6 | Dark brown | 79% | 203-205 | (61.67) | (3.88) | (11.99) | (5.44) |
| pNACAN   | 423.4        | Red      | 80%   | 181-183 | (70.91) | (4.05) | (9.92) | 7.25 |
| Co(pNACAN)₂ | 903.7 | Red-brown | 73%  | 194-196 | (66.45) | (3.57) | (9.30) | (6.52) |
| Ni(pNACAN)₂ | 903.5 | Brown  | 70%   | 233-235 | (66.47) | (3.57) | (9.30) | (6.50) |
| Cu(pNACAN)₂ | 908.3 | Dark red | 88%  | 261-263 | (66.11) | (3.55) | (9.25) | (7.00) |
Due to the importance of the azo derivatives in the pharmaceutical and medical fields, because of it their containing of many reactive groups affecting on cellular components, indeed its act as colorant agent entered in textile manufacturing and inks, few literatures were interested in the preparation of these derivatives, this is what prompted us to prepare such compounds. The amino chalcone (pNAC) was prepared via Clesan-Schmidt condensation in 10% basic alcoholic media, reaction end, followed by TLC (petroleum ether:ethyl acetate 4:1) that \((R_f=0.26)\).

The FTIR chart of (pNAC) observes the presence of the amine double str. Bands clearly at \((3390\) and \(3358\text{ Cm}^{-1}\) respectively), the chalcone congication bands at \((1687\text{ and }1517\text{ Cm}^{-1})[25]\, while the nitro group appeared at \((1344\text{Cm}^{-1})\) as in fig.1.

While, in the azo chalcone (pNACAI) chart, we indicated the absence of the amine bands and appearing new band at \((1468\text{ Cm}^{-1})\) related to azo group \((N=N)\), str. band at \((3412\text{Cm}^{-1}\) related to \((N-H)\) imidazole group) and the imidazole\((C=N)\) at\((1610\text{Cm}^{-1})\), These give an enhancement of preparation. As shown in fig.2.

**Fig.1** FTIR chart of pNAC.

**Fig.2** FTIR chart of pNACAI
The other ligand (pNACAN) chart, show the presence of the naphtholic (OH group) at (3340Cm\(^{-1}\)), and the (N=N)azo group at (1488Cm\(^{-1}\)).

Ligands are soluble in methanol, ethanol and highly soluble in (DMF,DMSO, Chloroform, CH\(_2\)Cl\(_2\) and acetone, while they are insoluble in water.

H\(^1\) NMR data :-

The proton nuclear magnetic resonance data, showed that the (pNACAI) ligand have:

1. 11.87 (s, 1H, imidazole proton).
2. 6.74 (d, 1H, )
3. 7.74 (d, 1H, ).
4. 2.5 (DMSO d\(_6\) protons).
5. 6.77-8.45 (m, Aromatic protons).

As in the fig.4
While the other ligand (pNACAN), have:
1. 10.19 (s, 1H, naphthol OH proton).
2. 6.94 (d, 1H, CO).
3. 7.75 (d, 1H, Ph).
4. 7.24 (CDCl₃ solvent signal).
5. 7.3-8.4 (m, aromatic protons). As shown in fig. 5

![Fig.5 H¹ NMR chart of pNACAN.](image)

**UV-Visible studies.** The two ligands (pNACAI and pNACAN) have a maximum absorbency at (454 nm and 460 nm) respectively, related to the electronic transition (π → π*). Indeed, others in the ultraviolet region, related to the (π → π*) electronic transition using ethanol as a solvent. As shown in fig. 6
Fig. 6 UV-Visible spectra of the ligands in ethanol at (1X10^{-5} M)

When these ligands mixed with the aqueous solution of TME ions (Co^{2+}, Ni^{2+} and Cu^{2+}), a vivid color obtained, indeed to red shifting occur on these spectra, this may attributed to the coordinating of the lone pairs of the donating atoms and the vacant orbitals of the ions and formation of the soluble complexes, these can observe in the mixing spectra fig. 7

From the UV-visible study data they can determine the complex formula by using the mole ratio method (M:L) ratio[26], from the results obtained, the mole ratio of (pNACAI) and (pNACAN) complexes are (1:2), they can prepare the solid complexes of the new ligands.

Fig. 7 Mixing spectra of the new ligands with divalent ion solutions at 5X10^{-5} M.
### Table. 2 Some spectroscopic data

| Compound | \( \lambda_{\text{max}} \text{ nm} \) | \( \log \varepsilon \) |
|----------|-------------------------------|------------------|
| pNACAI   | 454                           | 4.77             |
| [Co(pNACAI)\(_2\) (H\(_2\)O)\(_2\) ]Cl\(_2\) | 502 | 3.99 |
| [Ni(pNACAI)\(_2\) (H\(_2\)O)\(_2\) ]Cl\(_2\) | 498 | 3.98 |
| [Cu(pNACAI)\(_2\) (H\(_2\)O)\(_2\) ]Cl\(_2\) | 520 | 4.06 |
| pNACAN   | 460                           | 4.89             |
| [Co(pNACAN)\(_2\) ] | 474 | 4.00 |
| [Ni(pNACAN)\(_2\) ] | 484 | 4.03 |
| [Cu(pNACAN)\(_2\) ] | 510 | 3.84 |

The FTIR spectra of the solid (pNACAI) complexes show that an observable shifting in the azo (N=N) group and the imidazole (C=N) group towards lower frequency due to coordination of the nitrogen lone pair atoms to the vacant orbitals of the ions, indeed to the appearance of new band within 3300 Cm\(^{-1}\) related to the aqua hydroxyl of these coordinated to the central atom [27].

![Fig. 8 FTIR spectra of copper complex](image)

While the second ligand (pNACAN) complexes, also show the shifting of the azo group (N=N) to a lower frequency, indeed, to the disappearance of the hydroxy group due to the coordination of oxygen atom when the hydroxyl deprotonated.

![Fig. 9 FTIR of cobalt complex.](image)
Table 3 FTIR frequency data of the ligands and their complexes.

| Compound                  | Frequency in Cm⁻¹ | N-H | O-H | C≡N | N=N | M-N | M-O |
|---------------------------|-------------------|-----|-----|-----|-----|-----|-----|
| pNACAI                    | 3412              | ----| 1610| 1468| ----| ----| ----|
| [Co(pNACAI)₂(H₂O)₂]Cl₂    | Int. 3388cord.    | 1598| 1457| 543 |     |     |     |
| [Ni(pNACAI)₂(H₂O)₂]Cl₂    | Int. 3418cord.    | 1597| 1443| 520 |     |     |     |
| [Cu(pNACAI)₂(H₂O)₂]Cl₂    | Int. 3363cord.    | 1599| 1458| 574 |     |     |     |
| pNACAN                    | -----             | 3340| ----| 1488| ----| ----| ----|
| [Co(pNACAN)₂]             | -----             | -----| -----| 1450| 457 |     |     |
| [Ni(pNACAN)₂]             | -----             | -----| -----| 1446| 453 |     |     |
| [Cu(pNACAN)₂]             | -----             | -----| -----| 1427| 466 |     |     |

Int. = interfered with hydroxyl group frequency. Cord. = coordination aqua OH gp.

Electrical conductivity and magnetic susceptibility

The ionic properties of the compounds can be obtained from the conductivity measurements, that the charged species proportional to the molar conductivity and the complexes ionic degree can determine within measuring in different solvents.

Two types of solvents were used in this study (ethanol and dimethyl sulfoxide), the (pNACAI) complexes show an ionic properties (1:2) degree in these solvents, that indicate the presence of two chloride ion (out of coordination sphere), these will give these complexes the spiraling soluble character. While the (pNACAN) complexes owned a small value of conductivity in the same solvents i.e the nonionic properties of them, as in table 4.

Magnetic susceptibility[28] is another technique that used for deducing the complex geometry, this can enhance in the determination of the electronic configuration and oxidation state of the ion that the odd number of electrons deduce whether the complexes in high or low spin states. The magnetic susceptibility measurements for (pNACAI) complexes was:

- Cobalt complex shows a magnetic moment (4.31) BM this will agree with the presence of three odd electrons octahedral cobalt complex[29].

- Nickel complex gives (3.16)BM, i.e the existence of two odd electrons and this is compatible with the Nickle octahedral complex[30].

- Copper complex shows up (1.76) BM, a unique odd electron and this will agree with literature, for octahedral copper complexes[31].

The second ligand (pNACAN) complexes results as:

- Cobalt complex gives a (4.22) BM related the existence of three odd electrons as in tetrahedral cobalt complexes[32].

- Approaching to zero BM value for d⁸ complexes indicates no odd electron present in this complex, this will show for Nickle complex and this indicate the square planner geometry of this complex[33].

- Copper complex reveals a (2.19) BM, related to the absence of one electron of the copper tetrahedral complexes, the increment in value due to the orbital contribution of electrons to the magnetic moment[31].

Whole data outlined in table 4.
Table 4. The conductivity & magnetic moment data of the complexes.

| Complex                        | Molar conductivity | Magnetic susceptibility (B.M) |
|--------------------------------|--------------------|-------------------------------|
| [Co(pNACAI)$_2$ (H$_2$O)$_2$]Cl$_2$ | 110                | 4.31                          |
| [Ni(pNACAI)$_2$ (H$_2$O)$_2$]Cl$_2$ | 120                | 3.16                          |
| [Cu(pNACAI)$_2$ (H$_2$O)$_2$]Cl$_2$ | 115                | 1.76                          |
| [Co(pNACAN)$_2$]               | 20                 | 4.22                          |
| [Ni(pNACAN)$_2$]               | 34                 | Zero                          |
| [Cu(pNACAN)$_2$]               | 17                 | 2.19                          |

Conclusion
From the results obtained, they can conclude:
1. The first ligand (pNACAI) complexes have the octahedral di-cationic geometry as in the following figure:

![Fig. 10 Suggested geometry of (pNACAI) complexes](image_url)

Me = Co(II), Ni(II) and Cu(II)

1. The second legand (pANCAN) complexes were varied from the tetrahedral geometry of the cobalt & copper complexes to the square planar geometry of the nickel complex, as shown in the following figure.
Fig. 11 The suggested geometry of (pNACAN) complexes

SciFinder originality of the compound

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