# SYNTHESIS AND CHARACTERISATION OF 4-(4-NITRO-BENZENEAZO)-3-AMINOBENZOIC ACID COMPLEXES WITH Y(III) AND La(III) IONS

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**Keywords:** transition metal complexes, synthesis, spectral studies, azo dyes.

Coupling reaction of 4-nitroaniline with 3-aminobenzoic acid provided the corresponding bidentate azo ligand. The prepared ligand was identified by Microelemental Analysis, $^1$H-NMR, FT-IR, and UV-Vis spectroscopic techniques. Treatment of the prepared ligand with Y(III) and La(III) metal ions in 1:3 M:L ratio in aqueous ethanol at optimum pH yielded a series of neutral complexes with the general formula of $[M(L)_3]$. The prepared complexes were characterized by flame atomic absorption, Elemental Analysis (C, H, N), FT-IR, and UV-Vis spectroscopic methods, as well as conductivity measurements**.** The nature of the complexes formed were studied following the mole ratio and continuous variation methods; Beer's law obeyed over a concentration range of $1\cdot10^{-4}$ – $3\cdot10^{-4}$ M. High molar absorbtivity of the complex solutions were observed. In addition, the dyeing performance of the prepared ligand and their complexes were investigated on cotton fabric. The dyes were tested for light and detergent fastness. Biological activity of the ligand and complexes against three selected types of bacteria were also examined. Some of the complexes exhibited good bacterial activities.

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## Introduction

Azo compounds present a very important class of chemical compounds, receiving attention in scientific research.[1] They are highly coloured and have been used as dyes and pigments for a long time.[2,3] Synthetic dyes are produced in large amounts and are used in different industrial branches including the textile industry.[4] After processing, the excess of dye remains in the effluent, which must be treated before releasing into the environment.[5] The development of azo dyes with new structure has been a subject of interest, and many of these novel dyes are useful in commercial applications, for example in producing polyester, polyamide or polyacrylic fibres as well as their blends with other fibres.[6] Azo containing polymers, macromolecules with azo groups in the main chain or side chain polymers with azobenzene moiety, have good stability and usually show high glass transition temperature ($T_g$). Introducing azobenzene linkages in the polymeric main chain can improve thermal stability and allow application as an engineering plastic.[7] Azo compounds have a great biological activity as well as industrial importance.[8] Biological importance of azo compounds is well known for their use as antineoplastics, antidiabetics, antiseptic and other useful chemotherapeutic agents. It has been found that the activity of the azo linkage increases upon the incorporation of suitable heterocyclic moiety.[9] Metal complexes of azo compounds containing hetroaryl ring systems find various applications. These types of molecules have several advantages, for example the azo group is photocromic, redox responsive, and pH-sensitive.[10] In this work, we present the synthesis of an azo dye derived from 4-nitro-aniline as diazo component and 3-amino-benzoic acid as coupling agent. Complexes of this ligand with selected metal ions have also been studied and characterized physicochemically.

## Experimental

### Instrumentation

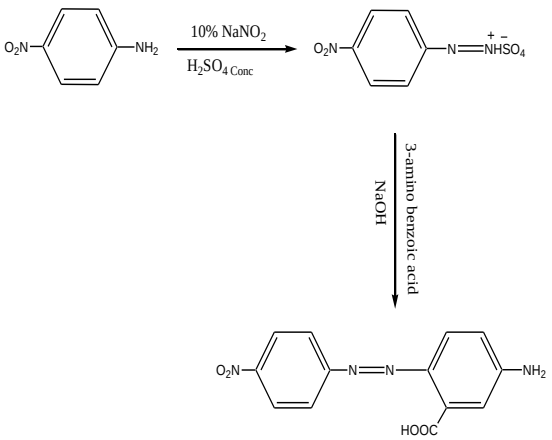
UV-Vis spectra were recorded on a Shimadzu UV-160A Ultraviolet-Visible Spectrophotometer. IR spectra were taken on a Shimadzu FT-IR-8400S Fourier Transform Infrared Spectrophotometer in the 4000–400 cm$^{-1}$ spectral region with samples prepared as KBr discs. Atomic absorption was obtained using a Shimadzu A.A-160A Atomic Absorption/Flame Emission Spectrophotometer. The $^1$H-NMR spectra were recorded on a Brucker-300 MHz Ultra Shield spectrometer at the University of Al-al-Bayt using DMSO as the solvent and TMS as the reference. Microelemental analysis (C, H, N) were performed at the Al-al-Bayt University, Jordan, using Euro vector EA 3000A Elemental Analyser. Conductivities were measured for $10^{-3}$ M solutions of complexes in ethanol at 25 ºC using Philips PW-Digital Conductimeter. In addition, melting points were obtained using Stuart Melting Point Apparatus.

**Materials and Reagents**

The following chemicals were used as received from suppliers: lanthanum chloride nonahydrate (98.8%) and yttrium nitrate pentahadrate (99.9%) (Merck), 4-nitroaniline and 3-aminobenzoic acid (B. D. H).

**Preparation of the Ligand**

According to a known general method,[11] 4-nitroaniline (0.342 g, 1 mmole) was dissolved in a mixture of sulphuric acid (2 ml), ethanol (10 ml) and distilled water (10 ml), and diazotized at 5 ºC with sodium nitrite solution. The diazo solution was added dropwise with stirring to a cooled ethanolic solution of 3-amino-benzoic acid (0.345 g, 1 mmole). 25 ml of 1 M sodium hydroxide solution was then added to the dark coloured mixture. The precipitate was filtered off and washed several times with 1:1 ethanol:water mixture, then left to dry. The reaction is shown in Scheme 1, while Table 1 describes the physical properties and elemental analysis.




**Scheme 1.** Synthesis of the azo ligand

**Buffer Solution**

Buffer solutions, covering the pH ranges of 4–9, were prepared as 0.01 M solutions of ammonium acetate in distilled water. The required pH was obtained by the addition of either ammonia solution or glacial acetic acid.

**Metal Salt Solutions**

A range of concentrations ($1\cdot10^{-5}$ - $1\cdot10^{-3}$ M) of the metal salt solutions were prepared by dissolving the appropriate weight of the metal salt in the buffer solutions.

**Ligand Solution**

The ligand solution was prepared by dissolving the required weight of the ligand in ethanol in a range of concentrations similar to that of the metal salt solutions.

**Dyeing Method**

The dyeing properties of the prepared ligand and their complexes were tested on "Hilla-Fine Textile State Company" using the Azoic Dyes Method. Dyes were applied on cotton fabric as 1% shade. The dyeing of the fabric was done at 15–20 ºC for 1 h, and at pH 10.

**Study of Biological Activity**

Three selected types of bacteria used include Escherichia Coli (E. Coli) as Gram Negative Bacteria, Staphylococcus Aureus (Staph. Aurous) as Gram Positive Bacteria and Pseudomonas Aeruginosa (Ps. Aeruginosa) in Neutrient Agar medium, using DMSO as a solvent and as a control, the concentration of the compounds in this solvent was $10^{-3}$ M, using disc sensitivity test. This method involves the exposure of the zone of inhibition toward the diffusion of micro-organism on agar plate. The plates were incubated for 24 hrs at 37 ºC.

**Preparation of metal complexes (general procedure)**

An ethanolic solution of the ligand (0.286 g,3 mmole) was added gradually with stirring to 0.120 g and 0.134 g of $Y(NO_3)_3\cdot5H_2O$ and $LaCl_3\cdot9H_2O$, respectively, dissolved in the buffer solution with the required pH. The mixture was cooled until dark colour precipitate was formed, filtered, and washed several times with 1:1 water:ethanol mixture, then with acetone.

**Table 1.** Physical Properties and Elemental Analysis of the Complexes.

| Compounds | Colour | M.P. ºC | Yield % | Analysis Calculated (Found) | | | |
|---|---|---|---|---|---|---|---|
| | | | | M % | C % | H % | N % |
| Ligand (L) | Orange | 224 | 77 | - | 54.54 (53.65) | 3.49 (3.21) | 19.58 (18.53) |
| $[Y(L)_3]$ | Deep brown | >360 | 83 | 9.43 (8.63) | 49.57 (48.28) | 2.86 (2.15) | 17.90 (16.83) |
| $[La(L)_3]$ | Red | >360 | 87 | 13.98 (12.86) | 47.08 (46.73) | 2.71 (2.07) | 16.90 (15.53) |

## Results and Discussion

The ligand was prepared by coupling 3-aminobenzoic acid with the approppriate diazotate in alkaline solution. The ligand is sparingly soluble in water, but soluble in organic solvents, and stable toward air and moisture.

The synthesized ligand was characterized by $^1$H-NMR, FT-IR, Elem. Anal. (C, H, N), and UV-Vis spectroscopic technique. The $^1$H-NMR spectrum of the 4-(4-nitro-benzene azo)-3-aminobenzoic acid in DMSO (Figure 1) shows multiplet signal at δ= 6.617–8.431 ppm, which refers to aromatic protons.[12] The signal at δ= 12.075 ppm appears due to the hydrogen atom of the carboxylic group.[13] The signal at δ= 3.887 ppm is assigned to δ($NH_2$) and the signal peak at δ= 2.50 ppm is referred to DMSO-$d_6$.[14]

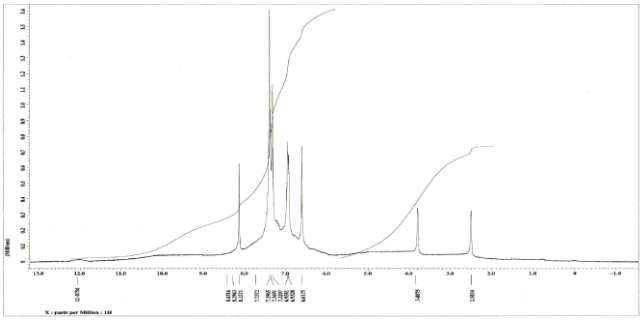


**Figure 1.** $^1$H-NMR spectrum of the azo ligand.

The UV-Vis spectrum of an ethanolic solution of the ligand ($10^{-3}$ M) displays mainly three peaks, the first and second peaks were observed at 251 nm and 242 nm and were assigned to the moderate energy π-π* transition of the aromatic rings (see Figure 2). The third peak was observed at 438 nm ($\lambda_{max}$) and was assigned to the π-π* transition of the intermolecular charge-transfer taken place from benzene through the azo group (-N=N).[15]

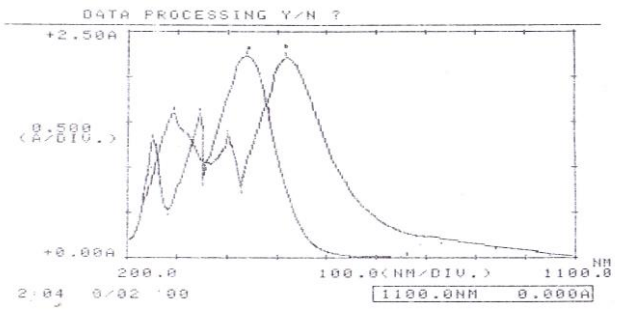



**Figure 2.** UV-Vis spectra of the solution containing the free ligand, L (a), and the $La^{III}$–L mixed solution (b).

Interaction of the metal ions ($Y^{III}$ and $La^{III}$) with the prepared ligand has been studied in solution; an aqueous-ethanolic solution was always prepared over wide molar concentration and acidity range. Colours of these mixed solutions were varied from brown to red.

The interaction of the metal ion with the ligand manifests itself in the absorption spectra by the appearance of two peaks at 589 nm and 563 nm. A great bathochromic shift in the visible region was detected in spectra of solutions of complexes with respect to that of the free ligand. The high shift in the absorption maximum ($\lambda_{max}$) gave a good indication for complex formation. Figure 2 shows a comparison between spectra of the ligand and $La^{III}$ mixed solutions.

From the wide studied range of molar concentrations ($10^{-5}$-$10^{-3}$ M) of the mixed solutions, only concentrations in the range of $10^{-4}$ M obey the Lambert-Beer's law, and only these solutions showed intense colour. A calibration curve was fitted to data points in the range of $1\cdot10^{-4}$ - $3\cdot10^{-4}$ M, which shows absorbance against molar concentration (Figure 3). Best fit straight lines were obtained with correlation factor of R>0.998.

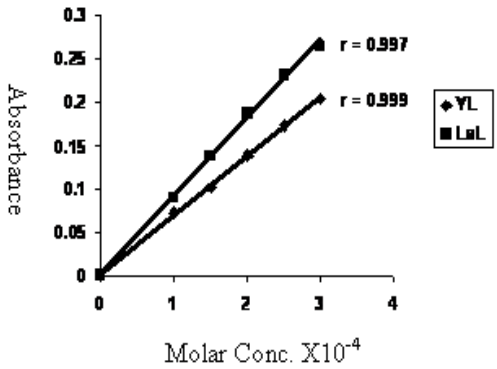



**Figure 3.** Linear correlation between molar concentration and absorbance.

The optimal concentration was chosen for complex solutions, and it was observed that the absorption maximum ($\lambda_{max}$) remained the same at different pH values. The influence of pH was also studied in the pH range of 4-9, and the absorbance–pH curves for each metal ion measured at $\lambda_{max}$ are plotted in Figure 4. Figure 4 shows selective pH-absorbance curves. The plateaus of the curves represent the completion of the reaction and consequently represent the optimum pH value.

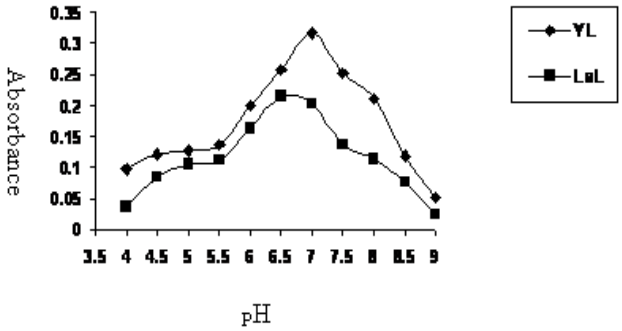



**Figure 4.** Effect of pH on absorbance ($\lambda_{max}$) for complexes.

The composition of complexes formed in solutions has been established by mole ratio and job methods. In both cases the results reveal a 1:3 metal to ligand ratio. A selected plot is presented in Figure 5.

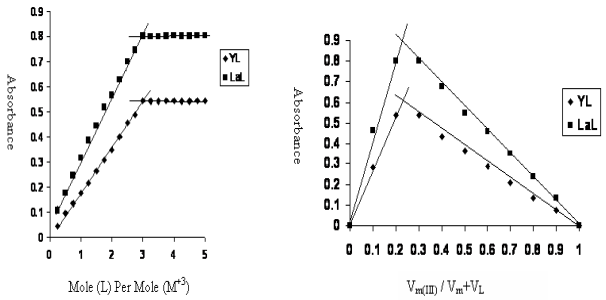



**Figure 5.** Mole ratio and Job methods for complexes' solutions.

Table 2 summarizes the results obtained, as well as conditions for the preparation of the complexes.

The solid complexes have been prepared by direct reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions at the optimum pH and in a M:L ratio of 1:3. The result of C.H.N analysis and the metal content of these complexes were in good agreement with the calculated values.

The molar conductance of $10^{-3}$ M ethanolic solutions of these complexes indicated their non-electrolytic nature;[16] data are presented in Table 2. The UV-Vis spectra of the prepared complexes dissolved in ethanol ($10^{-3}$ M) have been measured and the data obtained are included in Table 2. The large bathochromic shift of the absorption maximum ($\lambda_{max}$), assigned to ($\pi$-$\pi^*$) transition of the ligand, suggests the involvement of the ligand in the bond formation with the metal ion.

In order to study the bonding mode of the ligand with the metal ions, the FT-IR spectra of the free ligand and the prepared complexes have been compared, and data are tabulated in Table 3. The IR spectrum of the ligand (Figure 6) exhibited broad band at 3379 $cm^{-1}$, which was assigned to the stretching vibration of ν(OH) group. This band was absent in the spectra of all prepared complexes, which indicated deprotonation and involvement of the enol oxygen in chelation.[17,18] The bands at 3296 $cm^{-1}$ and 3116 $cm^{-1}$ appears due to the stretching mode of $\nu(NH_2)$. Since no change in these bands was noticed, the possibility that coordination occurs via the coordination of nitrogen atom of this group was excluded.[19] A significant change in the intensity and in position to lower wavenumbers was observed on complexation with metal ion for the strong band in the spectrum of the free ligand at 1666 $cm^{-1}$, which appears due to $\nu_{as}$(COO) asymmetric vibration (Figure 7). The band at 1558 $cm^{-1}$ in the spectrum of the ligand, which was assigned to the $\nu_s$(COO) symmetric vibration, suffered a great change to higher wavenumber on complexation with metal ion.[20,21] Band characteristic of the azo bridge vibration at 1489 $cm^{-1}$ shifted to lower frequency with change in shape in spectra of complexes, which is an indication of the engagement of this group in the coordination with the metal ion.[22,23] The appearance of new bands in the region of 470-578 $cm^{-1}$ are tentatively assigned to ν(M-N) and ν(M-O) (Metal-Ligand) stretching bands.[24,25]

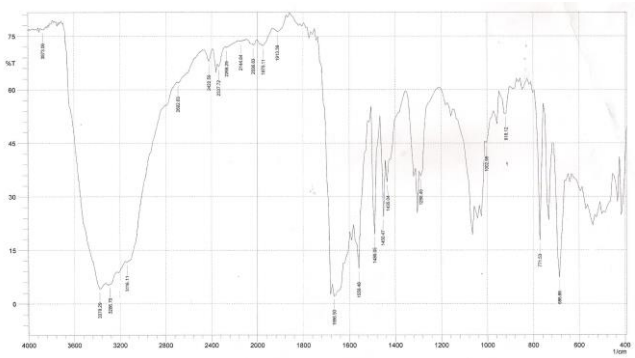


**Figure 6.** FT-IR Spectrum of the Ligand.

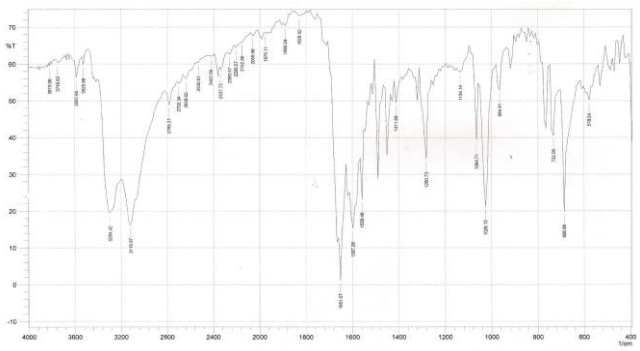


**Figure 7.** FT-IR Spectrum of $[Y(L)_3]$ Complex.

**Table 2.** Conditions for the preparation of complexes, and data of UV-Vis and conductance measurements.

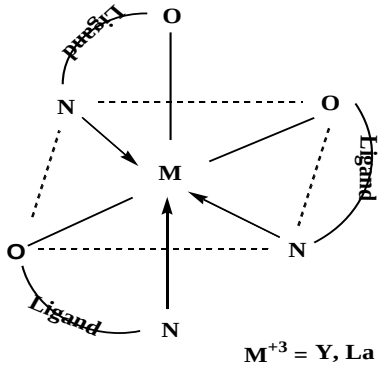
| **Compounds** | **Optimum pH** | **Optimum Molar Conc.** ($\cdot 10^{-4}$) | **M:L ratio** | $\lambda_{max}$ (nm) | **ABS** | $\epsilon_{max}$ ($L\cdot mol^{-1}\cdot cm^{-1}$) | $\Lambda_m$ ($S\cdot cm^2\cdot mol^{-1}$) in absolute ethanol |
|---|---|---|---|---|---|---|---|
| Ligand (L) | - | - | - | 438 | 2.232 | 2232 | - |
| $[Y(L)_3]$ | 7 | 2.5 | 1:3 | 589 | 1.598 | 1598 | 26.42 |
| $[La(L)_3]$ | 6.5 | 2 | 1:3 | 563 | 2.221 | 2221 | 27.13 |

**Table 3.** The main experimental wavenumbers of the ligand and their complexes (in $cm^{-1}$).

| Compounds | ν (OH) | ν($NH_2$) | $ν_{as}$(COO) | $ν_s$(COO) | ν(-N=N-) | ν (M-N) | ν (M-O) |
|---|---|---|---|---|---|---|---|
| Ligand(L) | 3379 br | 3296 br<br>3116 sh | 1666 s | 1558 sh | 1489 sh | - | - |
| $[Y(L)_3]$ | - | 3294 s<br>3116 s | 1651 sh | 1597 s | 1479 s | 578 w | 475 w |
| $[La(L)_3]$ | - | 3292 s<br>3114 s | 1656 s | 1570 sh | 1471 sh | 560 w | 470 w |

br = broad, s= strong, , sh = sharp, w = weak, as=asymmetric , s=symmetric

According to the results obtained, an octahedral structure has been tentatively suggested to these complexes (Scheme 1).




**Scheme 1**

The dyeing performance of the prepared ligand and their complexes was assessed on cotton fabric. The dyes were tested for light and detergent fastness. Thus all dyes showed very good dyeing properties, and they provided colours as orange, brown, and red with good brightness and depth on the fabric. Some of the dyeings are shown in Figure 8.

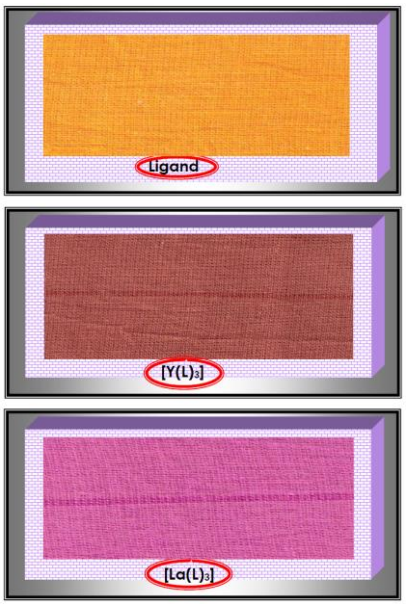
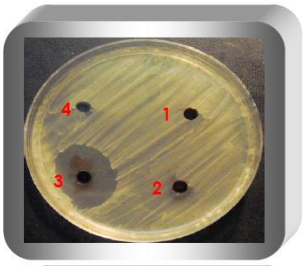



**Figure 8.** Samples of the textiles' dyeings prepared by using the ligand and its complexes.

Finally, the biological activities of the ligand and their complexes have also been tested against selected type of bacteria; the zone of inhibition of bacterial growth around the disc is presented in Figure 9. Table 4 shows the deactivation capacity against the bacteria specimen of the prepared compounds under study. The results show that the La-complex has a relatively strong deactivating capacity.

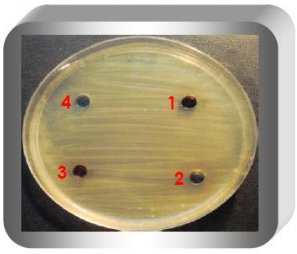
(A)
Staphlococcus aureus

1 – ligand (L)
2 – $[Y(L)_3]$ complex
3 – $[La(L)_3]$ complex
4 - solvent




(B)
Esherichia coli

1 – ligand (L)
2 – $[Y(L)_3]$ complex
3 – $[La(L)_3]$ complex
4 - solvent




(C)
Psedomonas aeruginosa

1 – ligand (L)
2 – $[Y(L)_3]$ complex
3 – $[La(L)_3]$ complex
4 - solvent

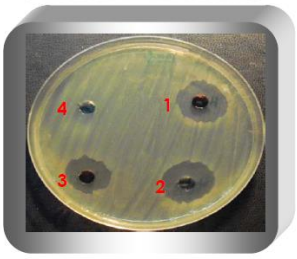



**Figure 9.** Inhibition zone of bacterial growth.

**Table 4.** Diameters (mm) of deactivation of bacteria for the ligand and its complexes.

| Compounds | Staphylococcus Aurous | Escherichia Coli | Pseudomonas Aeruginosa |
|---|---|---|---|
| Ligand(L) | – | – | ++ |
| $[Y(L)_3]$ | – | – | ++ |
| $[La(L)_3]$ | ++ | – | ++ |

(–) = no inhibition, (+) = inhibition diameter (6-8) mm, (++) = inhibition diameter (8-10) mm.

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