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### Synthesis and Characterization of Some New Metal Complexes 2-(4-nitrophenyl azo)-2,4-dimethylphenol.

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#### Abstract

The Ligand 2-(4-nitrophenyl azo)-2,4-dimethylphenol derived from 4-nitroaniline and 2,4-dimethylphenol was synthesized. The prepared ligand was identified by FT-IR and UV-Vis spectroscopic techniques. Treatment of the ligand with the following metal ions (  $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$ ) in aqueous ethanol with a 1:2 M:L ratio. Characterization of these compounds has been done on the basis of FT-IR and UV-Vis, as well as magnetic susceptibility and conductivity measurements. On the basis of physicochemical data tetrahedral geometries were assigned for the complexes.

**Keywords:** complexes, azo dyes, spectral studies.

#### Introduction

Azo compounds are a very important class of chemical compounds. receiving attention in scientific research. They are highly colored and have been used as dyes and pigments for a long time<sup>(1,2)</sup>. Furthermore, they have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium<sup>(3-6)</sup> toner<sup>(7,8)</sup> ink-jet printing<sup>(9,10)</sup> and oil-soluble lightfast dyes<sup>(11)</sup>. Recently azo metal chelates have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storage, nonlinear optical elements and printing systems<sup>(4,6,12)</sup>. Aromatic azo-compounds are coloured. Several of those compounds synthesized by the diazo-coupling are employed as dye-stuffs<sup>(13)</sup>. Colored compounds absorb some, but not all, wavelengths of visible light. When one looks at the light reflected from a colored object, the eye sees white light minus the wavelengths absorbed by the object. Therefore, a colored object appears as the color complementary to the wavelengths it absorbs<sup>(14)</sup>.

#### Experimental

##### Instrumentation

UV- Vis spectra were recorded on a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer. IR- spectra were taken on a Shimadzu, FT-IR- 8400S Fourier Transform Infrared Spectrophotometer in the 4000- 400  $\text{cm}^{-1}$  spectral regions with samples prepared as KBr discs. Atomic absorption was obtained using a Shimadzu A.A-160A Atomic Absorption/Flame Emission

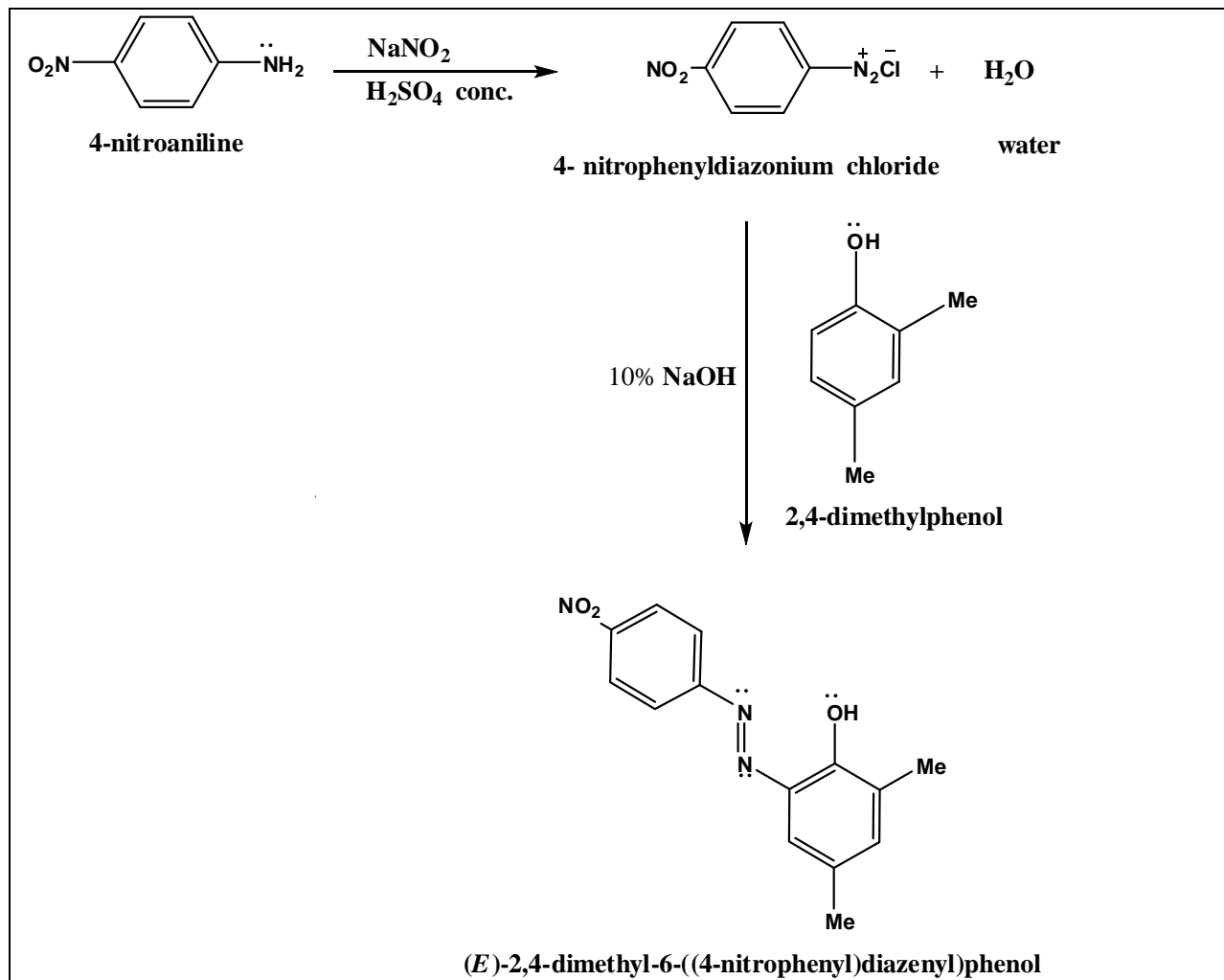
Spectrophotometer. Conductivities were measured for  $10^{-3}$  M solutions of complexes in ethanol at 25°C using Philips PW- Digital Conductimeter. Magnetic susceptibilities were performed by using Bruker Magnet B.M.6 instrument at 25°C. In addition, melting points were obtained using Stuart Melting Point Apparatus.

##### Materials and Reagents

The following chemicals were used as received from suppliers; cobalt chloride hexahydrate 98.8%, nickel chloride hexahydrate 99.9%, copper chloride dihydrate 98%, zinc chloride 98.8%, cadmiumchloride monohydrate 99% and mercury chloride 98% (Merck), 4-nitroaniline and 2,4-dimethylphenol (B. D. H).

##### Preparation of the Ligand<sup>(15)</sup>

(0.34g, 2.5mmole) of 4- nitroaniline has been dissolved in a mixture of (10 ml) sulphuric acid, (10 ml) ethanol and (10 ml) distilled water, and diazotized at (0- 5)C° with sodium nitrite solution. The diazo solution was added dropwise with stirring to a cooled ethanolic solution of (0.305g, 2.5mmole) of 2,4-dimethylphenol. (15 ml) of (10% M) sodium hydroxide solution was added to the dark yellow colored 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), (Table-1) describes the physical properties.



**Scheme 1.** Synthesis of the azo dye Ligand (L).

### Preparation of Metal Complexes (general procedure)

An ethanolic solution of the ligand (0.404g, 1mmole) was added gradually with stirring to the 0.0849g, 0.0679g, 0.1003g, and 0.134g (1mmole) of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{ZnCl}_2$ ,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{HgCl}_2$  respectively dissolved in distilled water. The mixture was cooled until dark color precipitate was formed, filtered and washed several times with (1:1) water: ethanol then with acetone.

### Results and discussion

The ligand (L) was prepared by coupling 2,4-dimethylphenol with the 4-nitroaniline in alkaline solution. The ligand (L) was sparingly soluble in water but soluble in organic solvents such as DMSO and DMF, stable toward air and moisture. Synthesized

ligand (L) was characterized by  $^1\text{H}$ NMR FT-IR and UV-Vis spectroscopic technique

The  $^1\text{H}$ NMR spectrum of the ligand in DMSO shows multiplet signal at  $\delta = 7.36 - 7.77$  ppm, which refers to aromatic protons.<sup>(16)</sup> A signal at  $\delta = 4.32$  ppm appears due to hydrogen atom of the phenolic group.<sup>(17)</sup> The signal at  $\delta = 3.33$  ppm is assigned to  $\delta(\text{CH}_3)$  and the signal at  $\delta = 2.50$  ppm referred to  $\text{DMSO-d}_6$ .<sup>(18)</sup>

Interaction of the metal ions  $\text{Cu(II)}$ ,  $\text{Zn(II)}$ ,  $\text{Cd(II)}$  and  $\text{Hg(II)}$  with the prepared ligand (L) has been studied in solution; an aqueous - ethanolic solution was always performed over wide molar concentration and acidity range. Colours of these mixed solutions were varied from brown or green.

The solid complexes have been prepared by direct reaction of alcoholic solution of the ligand (L) with the aqueous solution of the metal ions in a M:L ratio of 1:2. The metal content of these complexes were in good agreements with the calculated values.

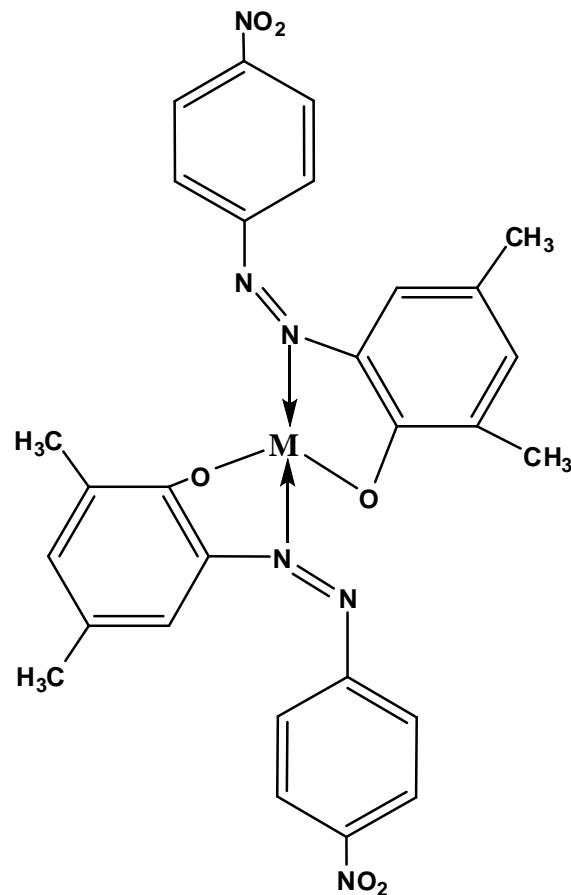
The molar conductance of  $10^{-3}$  M in ethanolic solutions of these complexes indicated their non-electrolytic nature;<sup>(19)</sup> data are presented in Table 1.

The effective magnetic moment (Table 2) of the Cu(II) complex at 1.83 B.M. This value refers to a paramagnetic (high spin) which has been reported for most tetrahedral geometry. In case of Zn(II), Cd(II) and Hg(II) complexes because of filled-d orbital, therefore the magnetic moment ( $\mu=0$ ) are diamagnetic<sup>(20)</sup>.

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 UV-Vis spectrum of an ethanolic solution of the ligand  $10^{-3}$  M displayed mainly two peaks, the first peak was observed at 350 nm was assigned to the moderate energy  $\pi-\pi^*$  transition of the aromatic rings. The second peak was observed at the 422 nm was referred to the  $\pi-\pi^*$  transition of intermolecular charge-transfer taken place from benzene through the azo group ( $-N=N$ )<sup>(21)</sup>. The spectrum of Cu(II) complex gave absorption peak at 269 nm due to charge transfer. The peak at 530 nm was caused by electronic transition<sup>(22)</sup>  ${}^2T_2 \rightarrow {}^2E$ . The spectra of Zn(II), Cd(II) and Hg(II) complexes showed absorption peaks at 362, 367 and 358 nm due to charge transfer. The absence of absorption peaks in the visible region indicated no (d-d) electronic transition happened, this is a good result for tetrahedral complex.<sup>(23)</sup>

In order to study the bonding mode of the ligand (L) with the metal ions, the FT-IR spectra of the free ligand (I) and the prepared complexes have been compared, and the data was tabulated in Table 3. The IR spectrum of the ligand (L) exhibited broad band at  $3462\text{ cm}^{-1}$ , which was assigned to the stretching vibration of  $\nu(\text{OH})$  group. This band was absent in the spectra of all prepared complexes, which indicated deprotonation and involvement of the enol oxygen in chelation<sup>(24)</sup>. Bands characteristic of the azo bridge vibration at  $1489\text{ cm}^{-1}$  and  $1429\text{ cm}^{-1}$  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<sup>(25)</sup>. The appearance of new bands in the region of  $411-530\text{ cm}^{-1}$  are tentatively assigned to  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$  (Metal-Ligand) stretching bands<sup>(26,27)</sup>.

According to the results obtained, a tetrahedral structure has been tentatively suggested to these complexes.



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

Comp.	M.wt. gm/mol.	Color	M.P. C <sup>o</sup>	M% (Found)
Ligand (L)	271	orange	245-247	-
[Cu(L) <sub>2</sub> ]	603.54	Dark brown	139-141	10.60 (9.85)
[Zn(L) <sub>2</sub> ]	605.39	brown	360>	10.74 (9.93)
[Cd(L) <sub>2</sub> ]	652.41	henna	360>	17.17 (16.83)
[Hg(L) <sub>2</sub> ]	740.59	Dark orange	360>	27.12 (26.68)

*Table (2) Conditions for the Preparation of the Complexes and UV-Vis, Magnetic Susceptibility and Conductance Measurements Data.*

Comp.	nm)λ (	$\nu^-$ (Cm <sup>-1</sup> )	E <sub>max</sub> (molar <sup>-1</sup> . cm <sup>-1</sup> )	$\Omega_M$ (S.cm.mol <sup>-1</sup> ) in Ethanol 10 <sup>-3</sup> M	eff $\mu$
Ligand(L)	422 350	23696.7 28571.4	26 54	-	-
[Cu(L) <sub>2</sub> ]	269 530	37174.7 18867.9	342 562	12.57	1.83
[Zn(L) <sub>2</sub> ]	362	27624.3	651	16.28	Dia
[Cd(L) <sub>2</sub> ]	367	27247.9	392	17.34	Dia
[Hg(L) <sub>2</sub> ]	358	27932.9	127	11.53	Dia

*Table (3) Characteristic stretching vibrational frequencies ( $\text{cm}^{-1}$ ) located in the FT-IR of the ligand (L) and its complexes*

Comp.	(O-H) <sup>v</sup>	(N=N) <sup>v</sup>	(M-N) <sup>v</sup>	(M-O) <sup>v</sup>
Ligand (L)	3462	1489, 1429	-----	-----
[Cu(L) <sub>2</sub> ]	-----	1456 , 1411	505	470
[Zn(L) <sub>2</sub> ]	-----	1427	518	497
[Cd(L) <sub>2</sub> ]	-----	1442 , 1411	530	440
[Hg(L) <sub>2</sub> ]	-----	1438 , 1421	503	411