



New Method for Preparation Of Azo Compounds and Study of

Its complexes with  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$  and  $\text{Hg}^{+2}$ .

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**Abstract:**

New method to prepare 4,4-Azodibenzoic acid with the ligand was identified by FT-IR and UV-Vis spectroscopic technique. Treatment of the ligand with the following metal ions ( $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Hg}^{+2}$ ) in aqueous ethanol with a 2:1 metal:ligand. The prepared complexes were characterized using flame atomic absorption, FT-IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements.

**Key words:** 4,4-azodibenzoic acid, ligands, conductivity.

**Introduction:**

Azo compounds are characterized by the azo group ( $-\text{N}=\text{N}-$ )<sup>(1)</sup>. Most are azo compounds contain only one group, but some contain two (diazo), three (triazole), or more<sup>(2)</sup>. Azo dyes for colored complexes with many metal ions in solution<sup>(3-5)</sup>. They are highly colored and have been used as dyes and pigments for a long time<sup>(6-8)</sup>. Furthermore, they have been studied widely because of their excellent thermal and optical properties in application such as optical recording medium<sup>(9-12)</sup>, toner<sup>(13,14)</sup>, ink-jet printing<sup>(15,16)</sup> and oil soluble light fast dyes<sup>(17)</sup>. Synthetic dyes are produced in large amounts and are used in different industrial branches including the textile industry<sup>(18)</sup>. The complexes of this ligand with some metal ions have also been studied and characterized physico-chemically.

**Experimental:**

**A-materials:** all chemicals used were of reagent grade and used without further purification  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  and  $\text{HgCl}_2$ . (Merck). 4-nitro benzoic acid (B.D.H).

**B-instrumentation:** FT-IR- spectra as KBr discs, in the range  $(4000-400) \text{ cm}^{-1}$  were obtained using a (shimadzu, FTIR.8400s) Fourier Transform Infrared Spectrophotometer. Electronic spectra were recorded in ethanol ( $10^{-3}\text{M}$ ) using (Shimadzu UV- 160A) ultraviolet-visible



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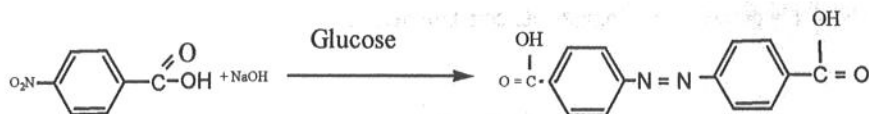
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Spectrophotometer. Magnetic properties were recorded using (Balance Magnetic Susceptibility Model MSB-MKI). The conductivities of ( $10^{-3}$ ) solution of metal complexes in ethanol were measured using (Philips PW-Digital Conductmeter). Atomic absorption measurement was obtained using (Shimadzu A-A-160A) Atomic absorption/Flame Emission Spectrophotometer. In addition melting point was determined by using (Stuart-Melting point Apparatus).

### Synthesis of 4,4-Azodibenzoic acid:

Thirteen grams of 4-nitrobenzoic acid (79mmol) was heated in a solution of 50 g of sodium hydroxide in 250 ml of water at  $50^\circ\text{C}$ . A solution of 100g of glucose in 150ml of occasional shaking. The reaction mixture was then cooled to ambient temperature and aerated for 8h. With vigorous stirring until orange-colored crystals were formed. The mixture was acidified with dilute acetic acid, and then the liberated diacid was filtered, washed with water and dissolved in hot potassium carbonate solution to get an orange colored solution. This solution was concentrated to get orange-colored crystals of potassium salt of diacid. On acidifying with acetic acid, 15g (79%) of rose-colored of 4,4-Azodibenzoic acid, was obtained  $\text{mp}=300\text{--}302^\circ\text{C}$  FT-IR (KBr): showed in Table (30).



### Synthesis of metal complexes

An aqueous solution of the metal salts containing 0.085 g, 0.068 g, 0.10 g and 0.135 g (1 mmole) of  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  and  $\text{HgCl}_2$  respectively was added gradually with stirring to ethanolic solution of the ligand (0.27 g, 2mmole). The mixture was cooled until dark color precipitate was formed, filtered and washed several times with (1:1) water: ethanol.

### Results and discussion:

The ligand was characterized by FT-IR and UV-Vis spectroscopy. The solid complexes were prepared by reaction of ethanolic solution of the ligand with the aqueous solution of the metal ions. The chloride ion and metal contents of these complexes were in good agreements with calculated value (Table-1) includes the physical properties. The molar conductance of the complexes as ( $10^{-3}\text{M}$ ) in ethanol solution indicating the electrolytic type<sup>(19)</sup> ratio (2:1) the data were recorded in (Table-1). The effective magnetic moments (Table-1) of the  $\text{Cu}^{+2}$  complex was (1.63 B.M.), this value refer to paramagnetic (high spin) which has been reported for most tetrahedral geometry. In case of  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$  and  $\text{Hg}^{+2}$  complexes because of filled d orbital, therefore the magnetic moments ( $\mu=0$ ) are diamagnetic<sup>(20)</sup>. The UV-Vis spectra data for the ligand and all metal complexes are listed in (Table-2). The UV-Vis spectrum of the ligand show peak at 345 nm due to  $\pi \rightarrow \pi^*$  electronic transition<sup>(21)</sup>. The electronic spectrum of



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$\text{Cu}^{+2}$  complex gave absorption peak at 395 nm due to charge transfer. The peak at 430 nm was caused by (d-d) electronic transition <sup>(22)</sup> type  $^2T_2 \rightarrow ^2E$ . The spectra of  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$  and  $\text{Hg}^{+2}$  complexes showed absorption peaks at 335 nm, 300 nm and 295 nm respectively were assigned to charge transfer. The absence of absorption peak in the range (371-1100 nm) indicated no (d-d) electronic transition happened (d<sup>10</sup>-system) in the visible region, which is good result for tetrahedral complexes <sup>(23)</sup>.

In order to study the binding mode of the ligand with the metal ions, comparison was made for the FT-IR spectra of the free ligand and those of the prepared complexes and the data was tabulated in (Table-3). The IR-spectrum of the ligand exhibited broad band at 3437  $\text{cm}^{-1}$  was assigned to  $\nu$  (OH) stretching frequency, absent this band in the spectra of all complexes, which indicated deprotonation and involvement of the enol o in chelating <sup>(24)</sup>. The spectrum of the ligand appeared band at 1693  $\text{cm}^{-1}$  due to  $\nu_{as}$  (COO), suffered a great change in the intensity and shifted to lower frequency was observed in the spectra of all prepared complexes. The band at 1575  $\text{cm}^{-1}$  refer to  $\nu_s$  (COO) vibration, suffered a great change to higher frequency was also observed in complexes spectra <sup>(25)</sup>. Band characteristic of the azo bridge vibration at 1409  $\text{cm}^{-1}$ , on complexes no change observed in the spectra, indicated that no coordination from this group <sup>(26)</sup>. The presence of coordination water <sup>(27)</sup> in the spectra of all complexes were suggested by very broad absorption around (3414-3430)  $\text{cm}^{-1}$ , the new bands observed at (540-491  $\text{cm}^{-1}$ ) are tentatively assigned to  $\nu$  (M-O) stretching bands <sup>(28,29)</sup>.

According to the results obtained an tetrahedral structure has been suggested of these complexes.

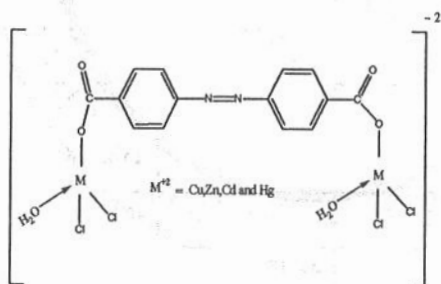


Table (1)- physical properties of the ligand and its complexes.

Compounds	Color	M.P.C	Yield %	M %	CL %	$\Delta m$ $\text{S.cm}^2.\text{mol}^{-1}$ In ethanol (10 <sup>-3</sup> M)	$\mu_{\text{eff}}$ B.M
Ligand	Rose	200 202	94	-	-	-	-



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$\text{Cu}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	Black-grey	٢٨٤ ٢٨٢	٧٣	22.29 (21.65)	24.73 (23.87)	79.65	1.63
$\text{Zn}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	Orange	٢٨١ ٢٨٣	٧٠	22.56 (21.42)	24.65 23.76	81.53	Dia
$\text{Cd}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	Graininess	٢٧٩ ٢٧٨	٦٩	33.43 23.91	21.19 20.53	88.71	Dia
$\text{Hg}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	Champagne	٢٤٦ ٢٤٥	٧١	47.40 46.51	16.74 15.75	75.97	Dia

Table (2) – electronic spectra data of the ligand and its complexes.

Complexes	$\lambda_{\text{nm}}$	ABS	Wave number( $\text{cm}^{-1}$ )	$\text{E}_{\text{max. 1.Mol}^{-1}.\text{cm}^{-1}}$
Ligand	345	1.370	28985.50	1370
$\text{Cu}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	٣٩٥ ٤٣٠	3.420 2.024	25316.45 23255.81	٣٤٢٠ ٢٠٢٤
$\text{Zn}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	٣٣٥	3.220	29850.74	٣٢٢٠
$\text{Cd}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	٣٠٠	3.316	33333.33	٣٣١٦
$\text{Hg}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	٢٩٥	3.156	33898.30	٣١٥٦

Table (3)- the infrared spectra for the ligand and its complexes.

Complexes	$\nu(\text{H}_2\text{O})$	$\nu(\text{OH})$	$\nu(\text{COO})$	$\nu(\text{COO})$	$\nu(\text{N}=\text{N})$	$\nu(\text{M}-\text{O})$
Ligand	-	3437 br.	1693 s.	1575 sh.	1492 sh.	-



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$\text{Cu}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	3420 br.	-	1685 sh.	1591 sh.	1492 sh.	540 w.
$\text{Zn}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	3422 br.	-	1680 s.	1600 sh.	1492 sh.	489 w.
$\text{Cd}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	3414 br.	-	1683 s.	1581 sh.	1494 sh.	491 w.
$\text{Hg}_2(\text{L})\text{CL}_4(\text{H}_2\text{O})_2$	3430 br.	-	1597 sho.	1579 sh.	1494 sh.	464 w.

br.=broad , s=strong , sh.=sharp , sho=sholder , w=weak.



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طريقة جديدة لتحضير مركب ازو ودراسة معقداته مع الايونات النحاس والكاديوم والزنك  
والزئبق

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الخلاصة

لقد تم تحضير مركب ٤،٤-ازو داي بنزويك اسيد بطريقة جديدة تختلف عن طرق تحضير مركبات الازو كأملاح الدايازونيوم. ثم شخص الليكاند المحضر بوساطة اطياف الاشعة تحت الحمراء وفوق البنفسجية -المرئية. وتم مفاعلة الليكاند مع الايونات الفلزية (النحاس والكاديوم والزنك والزئبق) بنسبة فلز : ليكاند (١:٢) في وسط ايثانول - ماء. شخصت المعقدات المحضرة باستخدام تقنية الامتصاص الذري اللهب. اطياف الاشعة تحت الحمراء والاشعة فوق البنفسجية - المرئية فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية.



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