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RESEARCH ARTICLE

Synthesis and Identification of novel azo-1,3,4-Thiadiazole Derivative and using to Spectrophotometric Determination for some of Transition metal Complexes

Shaimaa Adnan[1], Shaimaa Mohsen[2], Hayder Obaid Jamel[3]
[1,2]Department of Chemistry, College of Education, University of Al-Qadisiyah, Diwaniyah, Iraq
[3]Department of Pharmaceutical Chemistry, College of Pharmacy/University of Al- Qadisiyah, Diwaniyah, Iraq
*Corresponding Author E-mail: **shaimaa.adnan@qu.edu.i , shemaadnan@yahoo.com,**
shymaa.essa@qu.qu.iq, shaimaamohsen79@yahoo.com

ABSTRACT:
This search includes synthesis of ligand by a two-step, the first react between 4-hydroxy benzaoic acid and thiosemicarbazide to form compound (1) [4-(5-amino-1, 3, 4-thiadiazol-2-yl) phenol], the second step is coupling of diazonium salt [5-(4-hydroxyphenyl)-1, 3, 4-thiadiazole-2-diazonium] with 2-hydroxy-5-sulfobenzoic acid in basic ethanolic media to get compound (2) [(E)-2-hydroxy-3-((5-(4-hydroxyphenyl)-1, 3, 4-thiadiazol-2-yl) diazenyl)-5-sulfobenzoic acid] which characterized by FT-IR ,^{1}H NMR and ^{13}C-NMR , after that used for the spectrophotometric determination of cadmium Cd (II) and lead Pb (II). This method was simple, rapid, sensitive, and selective for reaction between cadmium and lead with the reagent. The maximum absorbance observed at 450 nm and 495 nm for Cd(II) and Pb(II) respectively. The molar absorptivity and sandell's sensitivity for cadmium (II) and lead (II) complexes are 4.5077×10^{-4}, 2.9709×10^4 L.mol^{-1}. cm^{-1} and 0.0212, 0.0353μg/cm^2 respectively. The stability constant of 1:2 [M:L] complexes of Cd(II) and Pb(II) are 3.13×10^5 and 1.45×10^5 L.mol^{-1} respectively. The linear range of 0.1-9 µg mL^{-1}, 0.2-12 µg mL^{-1} along with limit of detection 0.059 µg mL^{-1}, 0.102 µg mL^{-1}, relative standard deviation for seven replication measurements (5 µg Cd mL^{-1} and 5 µg Pb mL^{-1}) of (0.059%) and (0.102%) ,and the recovery range of (98.6) and (99.2) were obtained for Cd(II) and Pb(II) ions respectively.

KEYWORDS: 1, 3, 4-thiadiazole, Azo, spectroscopy, lead and cadmium.

INTRODUCTION:
Heterocyclic compound specially five- membered important classes using in biological activities and medicinal properties, in this research, we prepare 1,3,4-thaidiazole derivatives and insertion azo group to form 1,3,4-thaidiazole-azo derivative which contains very effective groups such as(hydroxyl, carboxyl, sulfonyl), this classes of azoles used as antifungal, antiviral, anti-inflammatory, antimicrobial, and anticancer [1-3].

The heavy metals lead and cadmium, lead the cause to many serious diseases in addition to lead poisoning is the cause of severe anemia.

Several techniques such as voltammetric, flame atomic absorption and spectrophotometric methods have been used for the determination of the ion in different samples. Among this, UV-Visible spectrophotometry is the most commonly used techniques for Pb(II) [4].

The Cadmium is considers from the essential elements, and its has a wide use in biological effects due to the biological activity and behaving [5].

Apparatus:
(FTIR) Spectra ((4000-400cm^{-1})) in (KBr) disk were recorded on a (SHIMADZU FTIR-8400S) fourier transform, While(^{1}HNMR) spectra were recorded using a Braker (400MHz) spectrophotometer in Department of chemistry, kashan university, Iran. Electronic spectral were recored on (shimadzu) UV-160 (A) Uletr-Visible Spectrophotometer using 1 cm quartz cells, pH – meter

was used to adjusted and measure the pH of the solution.

synthesis of 4-(5-amino-1,3,4-thiadiazol-2-yl)phenol compound (1):

In a (100 ml) round bottom flask was placed a mixture of (0.01mole) of 4-hydroxybenzoic acid and (0.01mole) thiosemicarbazide in (8 ml) of phosphorous oxychloride, The reaction mixture was (3h), after that the solution cooled and add (40ml) distill water ,after that refluxed (4h). The reaction mixture was cooled and kept at(24hr). the solvent was then removed and the resulting solid was recrystallized from ethanol to give compound (1)[6].

Synthesis of (E)-2-hydroxy-3-((5-(4-hydroxyphenyl)-1,3,4-thiadiazol-2-yl) diazenyl)-5-sulfobenzoic acid (compound 2) :-

(0.01 mol) 4-(5-amino-1,3,4-thiadiazol-2-yl)phenol was dissolved in (10)ml of con. HCl then (30 ml) of cold distilled water was added ,this solution was (0.75 gm) of sodium nitrate in (20 ml) of distilled water was added dropwise at (0-5)°C and left stirring to stand (30 min) . the resulting diazonium chloride solution was added dropwise with cooling to a solution of 2-hydroxy-5-sulfobenzoic acid (0.01mol) dissolved in (100ml) alkaline ethanol . The yield was 74 % of purple crystals .The mixture was allowed to stand and nevralied with dilute HCl at PH=6.The product was filtered off and recrystallized from hot ethanol and then dried in air [7].
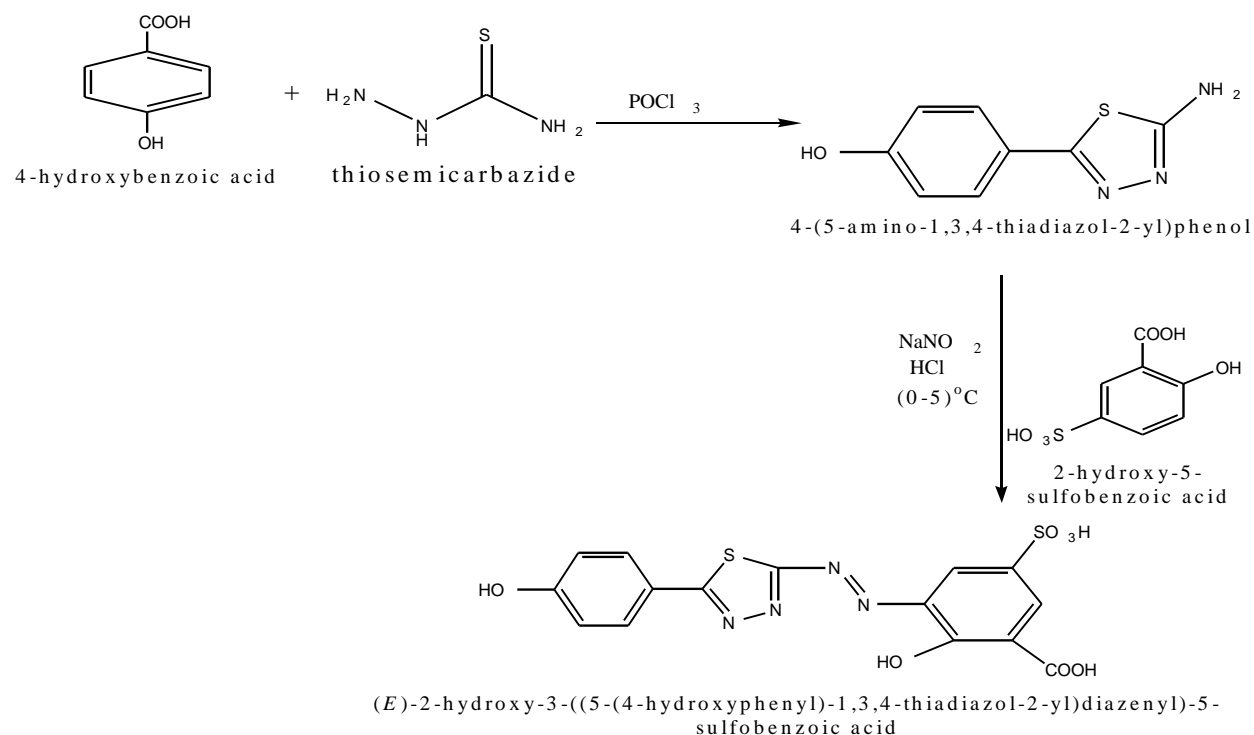
Scheme (1) synthesis of (E)-2-hydroxy-3-((5-(4-hydroxyphenyl)-1,3,4-thiadiazol-2-yl)diazenyl)-5-sulfobenzoic acid

Reagents and Solutions:

All the chemicals used were of analytical reagent grade, and were used without further purification. Ethanol were purchased from (GCC, England) . A 1.0×10^{-4} mol L^{-1} was prepared by dissolving (0.0106 g) of(E)-2-hydroxy-3-((5-(4-hydroxyphenyl)-1,3,4-thiadiazol-2-yl)diazenyl)-5-sulfobenzoic acid (compound 2) in 250 mL absolute ethanol. Stock solutions of Pb(II) and Cd (II) ions (1000 mg L^{-1}) were prepared by dissolving (0.1598 g) of Pb(NO$_3$)$_2$ (BDH) and (0.197 g) of CdCl$_2$.H$_2$O (Merck) in 100 mL deionized water, respectively. Working standard solutions of each metal ion were freshly prepared by appropriate dilutions of the stock standard solutions. The pH of the medium (3-9)

were adjusted with ammonium acetate (0.01 mol L^{-1}) – ammonia – glacial acetic acid buffer solution .

General procedure:

In to a 10 mL calibrated flask , transfer 5 mL of sample solution containing less than 100 µg.ml^{-1} of Cd(II) and adjust the pH to 5.5 with ammonium acetate buffer, add 3 ml 1.0×10^{-4}M ethanolic reagent solution and diluted to the mark with deionized water. The absorbance of the resultant solution was measured after 10 min at 450 nm at 25 C° against the corresponding reagent blank prepared under identical conditions but without cadmium. The same procedure for lead (II) but add 2 ml 1.0×10^{-4}M ethanolic reagent solution and diluted to the

mark with deionized wate at(pH 6) and the absorbance of the result solution after 10 min at 495 nm.

RESULTS AND DISCUSSION:
Infrared spectra:
The infrared spectrum data of compound(1) shows absorption at (3348) cm^{-1} for U (O-H) phenol which Overlapped with absorption pack of (NH_2) group , The band at (1635) cm^{-1} , which due to (C=N) thiadiazole ,also shows band at (1600) cm^{-1} for (C=C)aromatic ring , and band for (C-S) at (1157)cm^{-1} .
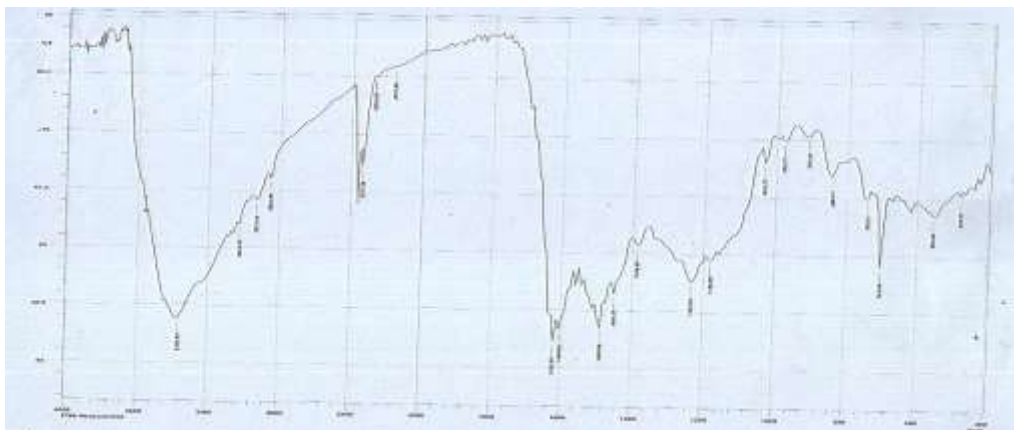

Fig (1) FT-IR spectrum of compound (1)

The infrared spectrum data of ligand show absorption at (3448) cm^{-1} for (O-H) carboxylic acid, (1480) cm^{-1} for (N=N-) azo group ,(1533) cm^{-1} ,(C=N) pyridine ,and show band at U (1630) cm^{-1} for (C=C)aromatic ring , and band for (C-S) a at (1157)cm^{-1} .

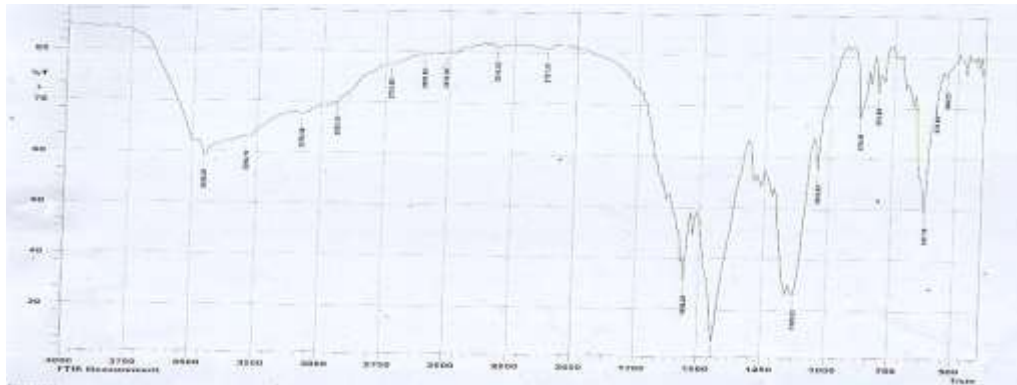**Fig (2) FT-IR spectrum of the Reagent**

New weak bands in the region (550-400)cm^{-1} occurring in the complexes spectra, these bands did not spectrum of the free reagent may attributed toU(M-O)and U(M-N)show in table (2) [8-10].
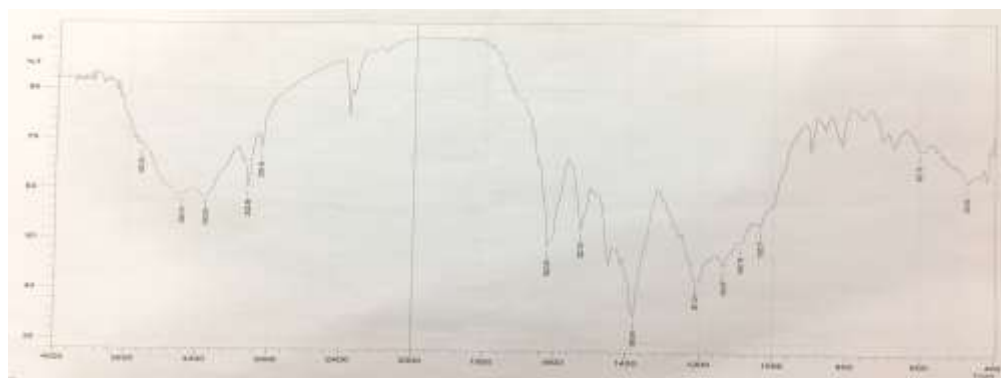

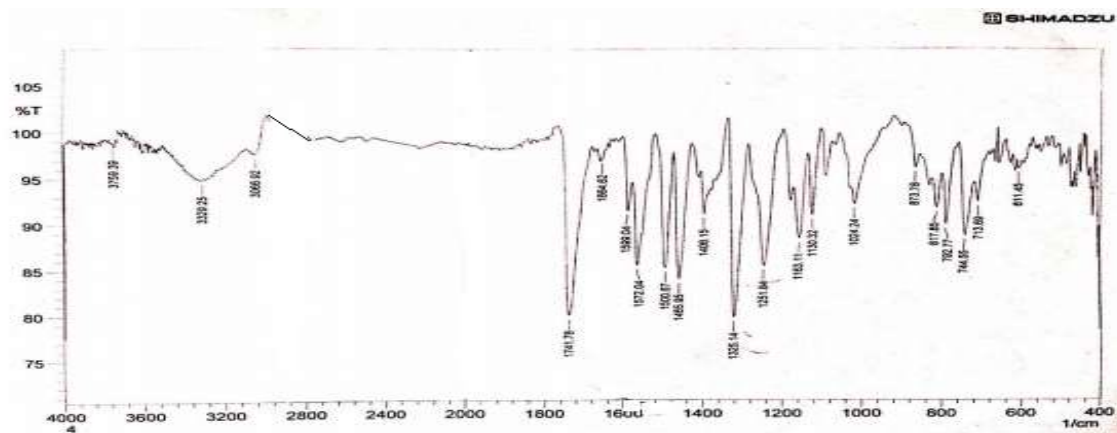**Fig (3) FT-IR spectrum of the Cd complex**

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Fig (4) FT-IR spectrum of the Pb complex

¹H NMR Spectra For compound (1):

The¹H-NMR(DMSO-d_6) spectrum data of compound show δ:6.8-7.5 (m, 4H, Ar-H), 5.52(m,2H, NH$_2$), 4.8(s, 1H.OH).
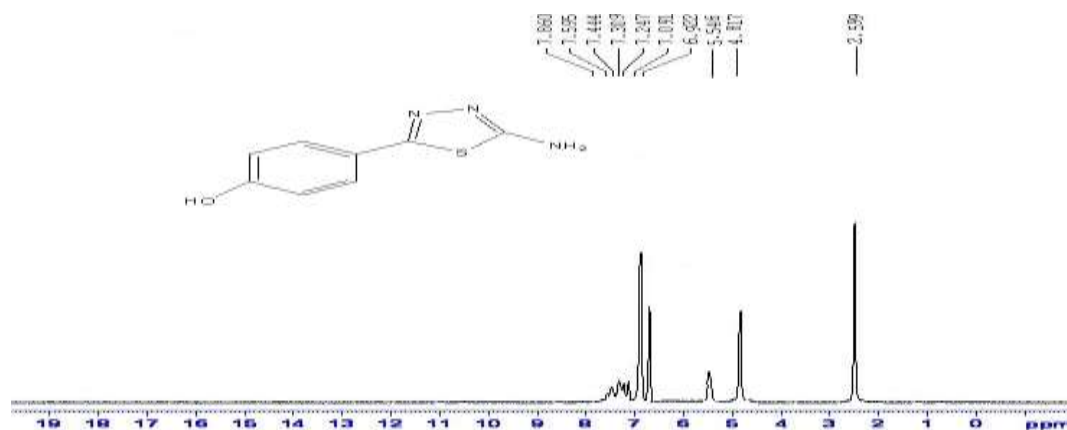

Fig (5) ¹H-NMR Spectrum of Compound(1)

¹H-NMR Spectrum of L

The¹H-NMR(DMSO-d_6) spectrum data of L shows δ:7.09-7.99 (m, 6H, Ar-H), 10.99 (m,1H, CO<u>OH</u>), 10.19 (m,1H, HOCC-C-<u>OH</u>), 6.13 (m,1H, SO2-OH), 5.57 (m,1H, Ar-<u>OH</u>)[(19,20)] .
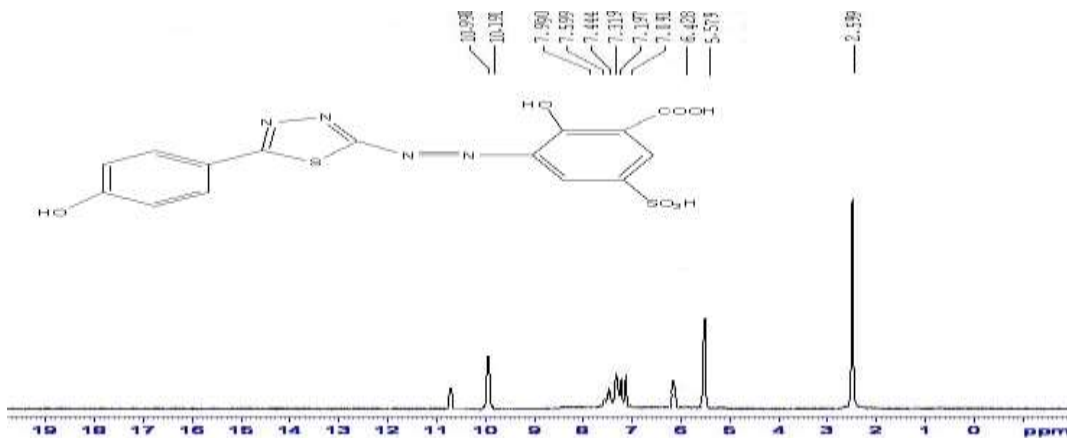

Fig (6) ¹H-NMR Spectrum of L

¹³C-NMR Spectrum of compound (1)

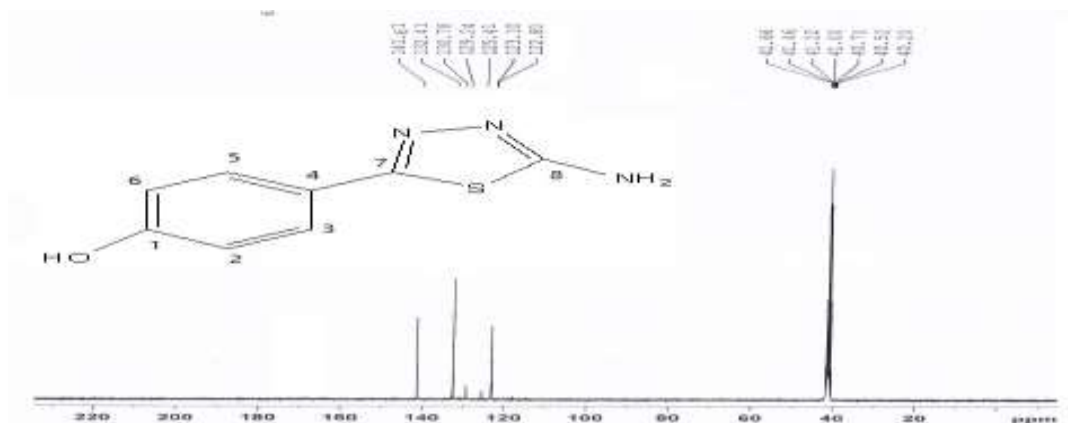The¹³C-NMR(DMSO) spectrum data of compound (1) show δ:141.6 (C7, 132.4 (8), 129 (C1), 125.4 (C2,C6), 122(C3,C5.).

Fig (7) ¹³C-NMR Spectrum of Compound(1)

¹³C-NMR Spectrum of L

The¹³C-NMR(DMSO) spectrum data of L shows δ:156 (C15), 138.2 (C8), 132(C14), 131(C1), 130(C11), 130.1 (C11), 126.4 (C10), 124.1(C8), 122.9(C9), 121.4(C12), 121.3 (C3,C5), 118.3(C2,C6), 113.3(113).
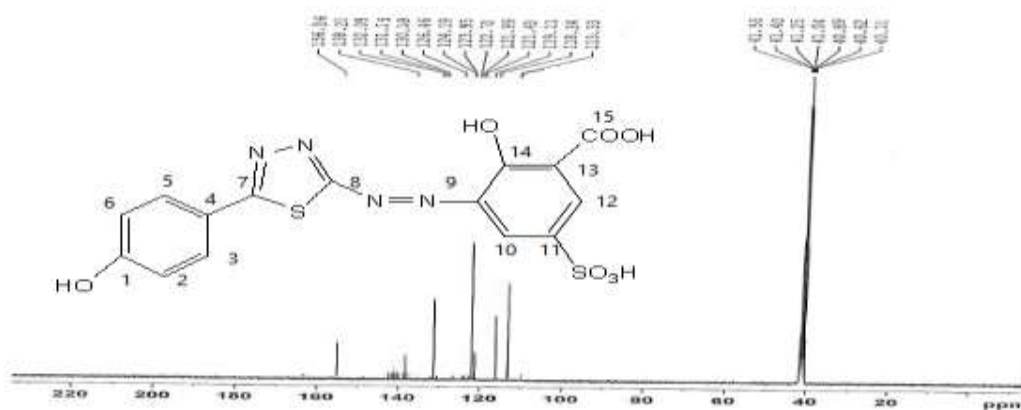

Fig (8) ¹³C-NMR Spectrum of L

Absorption spectra and characteristics of the complex:

The UV- Vis spectrum of an ethanolic solution of the reagent (E)-2-hydroxy-3-((5-(4-hydroxyphenyl)-1,3,4-thiadiazol-2-yl)diazenyl)-5-sulfobenzoic acid (1×10^{-4}M) showed peak (λmax) was observed at the (407 nm) due to the (π-π*) from aromatic ring through the azo group (charge transfer) was referred to the n- π* transition of intermolecular charge- transfer taken place from benzene through the azo group(-N=N-) Interaction of the metal ions Cd(II) and Pb(II) with the reagent has been studied in aqueous ethanolic solution. A bathochromic shift of Cd(II) and Pb(II) complexes show the absorption maxima of 450 and 495 nm referred to (charge transfer) with molar absorptivities (ε)of 4.5077×10^{-4}L.mol⁻¹.cm⁻¹and 2.9709×10^{-4}L.mol⁻¹.cm⁻¹obtained respectively while the reagent gave the absorption maxima of 407 nm The wave length different(Δ λmax) is (43-88 nm), a great bathochromic shift in the visible region has been detected in the complex solutions spectra with respect to that of the free reagent. The high shift in the (λmax) gave a good indication for complex formation.

Method Validation:

Under the optimized conditions, the calibration graphs were constructed by plotting the absorbance signal against the concentrations of each analyte subjected according to the general procedure. The solutions were transferred into the optical cell of 1-cm for the measurement of each metal ion spectrophotometrically at the respective absorption maxima against a reagent blank prepared under similar conditions. The calibration data and some analytical parameters are summarized in Table(1).

Table (1): Analytical data and some analytical parameters of the proposed method for determination of Cd(II)and Pb(II))

Analytical Parameter	Cd (II) / ppm	Pb (II) / ppm
λ$_{max}$ (nm)	450	495
Regression equation	Y=0.0472X+0.1501	Y=0.0283X+0.0178
Molar absorptivity(L.mol⁻¹.cm⁻¹)	4.5077×10^{-4}	2.9709×10^{-4}
Sandell Sensitivity(μg.cm⁻²)	0.0212	0.0353

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Correlation coefficient(r)	0.9929	0.9891
Detection Limit(D.L)	0.059	0.102
Linear dynamic range	0.1 - 9	0.2 - 12
Standerd deviation	0.0015	0.001
Relative. Standard. Deviation %	0.393 (N=7)	0.68 (N=7)
Percent Relative error	1.4	0.8
Percent Recovery	98.6	99.2
Composition of complex (M: L)	1:2	1:2

(N=no. of determination)
Optimization of Procedure:
Effect of pH
The effect of pH on formation of the (Cd(II),Pb(II))-complexes was determined by recording their absorbance signals at λmax , over the range of 2-10,using different pH buffer solution (NH3+ CH₃COOH). The results are shown in Fig.10.
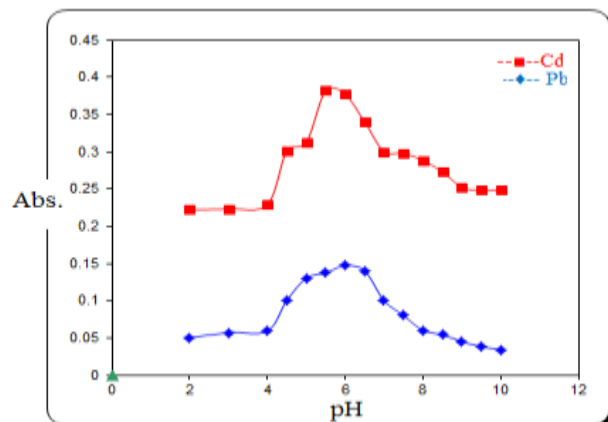

Fig.(9): Effect of pH on the formation of complexes formed with (Cd(II) and Pb(II).

As can be seen in Fig.(10), the absorbance first increased with increasing pH and reached a maximum at pH 5.5for Cd(II) and 6 for Pb(II) complexes. The absorbance gradually decreased because of partial dissociation of the complexes at higher pH. Therefore, pH 5.5 and 6 were selected as the optimum pH's for complete formation of for Cd(II) and Pb(II) complexes, respectively.

The stability of the complexes at different times and different temperatures:
The absorbance of the complexes reaches a maximum value within 10 min are sufficient for the maximum absorbance of Cd(II) and Pb(II), respectively, and remains stable for 24 hour. The effect of the temperature for the complexes was studied in the range (20-70) C⁰, the maximum and constant absorbance were obtained in the range (20-40)C⁰for each Cd(II) and Pb(II),it was decrease in the temperature more than 40C⁰ for Cd(II) and Pb(II)) because the complexes will be dissociated or evaporated in these temperatures.
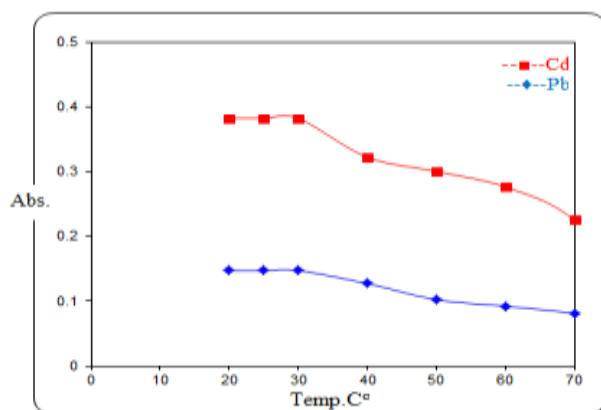

Fig.(10): Effect of the temperature on the absorbance for complexes formed with Cd (II)and Pb (II)
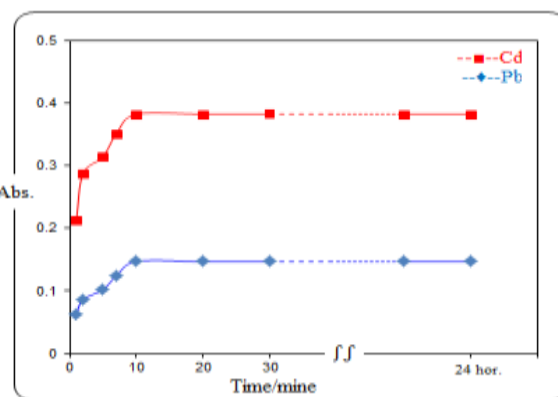

Fig.(11): Effect of time on the absorbance for complexes formed with Cd (II)and Pb (II).

Composition of complex and stability constant:
The composition and the stability constant were evaluated by both of the mole ratio and continuous variation the methods (fig.13 and 14). Both methods showed that the molar ratio of (Cd(II) and Pb(II) ions are 1:2 (metal: ligand) at pH 5.5 and 6 to reagent (E)-2-hydroxy-3-((5-(4-hydroxyphenyl)-1,3,4-thiadiazol-2-yl) diazenyl)-5-sulfobenzoic acid. The stability constant is found to be 3.1×10^5 L.mol^{-1} and 1.4×10^5 L.mol^{-1} for Cd(II) and Pb(II) respectively, and (α) of complexes were found to be (0.13 L.mol^{-1}) and (0.16 L.mol^{-1}) respectively by using the following equations[11]:

$$\mathbf{K_{st}} = \frac{1}{\mathbf{K_{inst}}} \qquad (1)$$

$$K_{inst} = \frac{(\alpha C)(n\alpha C)^n}{C(1-\alpha)} \ .$$
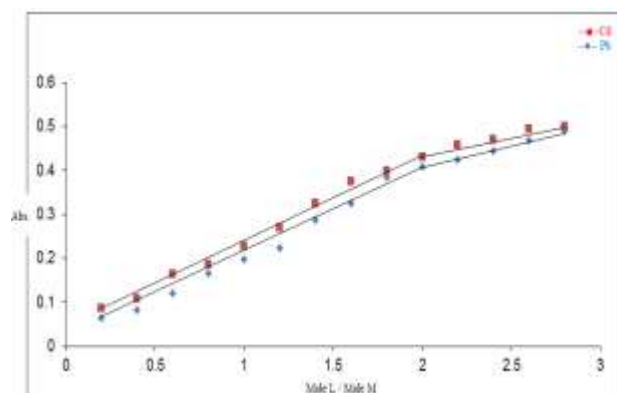
$$\alpha = \frac{A_m - A_s}{A_m} \qquad (2)$$

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Where:

α=degree of dissociation.

c =total concentration of the complex , n =mole ratio =(2 to Cd(II),2 to Pb(II)).

Em= absorbance of a solution containing reagent two times excess than the amount of cadmium and Lead.

Es= absorbance of a solution containing a stoichiometric amounts [reagent].

[cadmium and Lead].

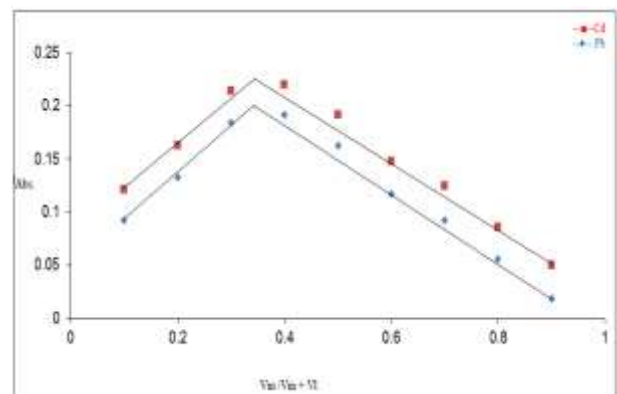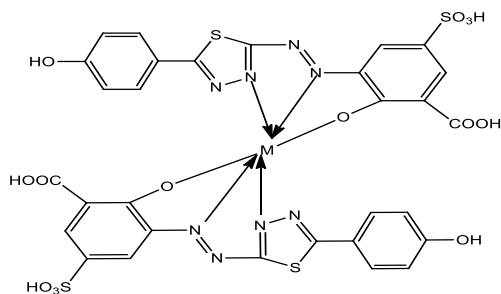**Fig(12): Mole ration method for Pb(II)-complex at pH=6 and Cd(II)-complex at pH=5.5**

Fig.(13): Continuous variation method for Pb(II)-complex at pH=6 and Cd(II)-complex at pH=5.5.

Suggestion of structural formula of complexes:

From the obtained results of metal to reagent ratio, FTIR-Spectrum ,and depending on Imidazol compounds properties; the following structure can be suggested:

M= Cd, Pb

Fig.(14): structural formula of complexes

CONCLUSIONS:

In this paper, reagent reacts with Cd(II) and Pb(II) and forms water insoluble complexes. Spectrophotometric method has been found to be quite simple, rapid, cheap, less time consuming and gave reproducible results, than most of the other methods, applicable for the determination of these metals in the presence of each other, which makes it an alternative to the existing methods for the determination of these metal ions.

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