

## Preparation , Identification of Co(II),Ni(II) and Cd(II) with the New Ligand 5-((2,4-dichlorophenyl)azo)-2,2-dimethyl-1,3-dioxane-4,6-dione (DPOD)

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### Abstract

The New ligand of 5-((2,4-dichlorophenyl)azo)-2,2-dimethyl-1,3-dioxane-4,6-dione (DPOD) have been prepared . Three chelate complexes Have also been prepared by reacting this ligand with the metal ions Co (II),Ni(II) and Cd(II). The preparation has been conducted after fixing the optimum conditions of concentration U.V- visible spectra of these complexes solutions have been studied for a range of pH and concentrations which obey Lambert-Beers Law .The structures of complexes are deduced according to mole ratio method which were obtained from the spectroscopic studies of the complex solutions .The ratios of metal: ligand obtained are (1:2) for all complexes ions .(UV-Vis) absorption spectra of ethanolic solution of complexes showed bathchromic shift , as compared with that of free ligand .The infrared spectra of the chelating complexes have been studied ,this may indicate that coordination between the metal ions and the prepared ligand takes place .The conductivity measurements ,the percentage of metal ions of the complexes were determined ,depending on these results , in addition to, the proposed geometrical structures of the complexes of Co (II), Ni(II), Cd(II) ions are octahedral .

**Keywords:** Preparation, Identification , new azo ligand, metal complexes .

### الخلاصة

تم تحضير الليكاند الجديدة ٥-((٢,٤-داي كلوروفينيل)ازو)-٢,٢-داي ميثيل-١,٣-داي أوكسان-٤,٦-داي أون كما تم تحضير معقدات هذه الليكاند مع ايونات الكوبلت (II) والنيكل (II) والكاديوم (II) ، وقد تم التحضير بعد تثبيت الظروف الفضلى للتركيز من خلال دراسة اطياف الاشعة فوق البنفسجية - المرئية لمحاليل مزج هذه الايونات مع محاليل الليكاند ولمدى واسع من التراكيز الخاضعة لقانون لامبرت - بير . وقد تم التعرف على التراكيب المحضرة للمعقدات عن طريق ايجاد النسبة المولية لعلاقة ( الفلز : الليكاند ) بوساطة دراسة اطياف (UV-Vis.) لمحاليل خلط الايونات الفلزية مع الليكاند ، وبينت الدراسة انها ( 2 : 1 ) لكل المعقدات . شخص الليكاند والمعقدات الصلبة المحضرة بالوسائل التحليلية والطيفية المتاحة فقد تم تشخيصها بوساطة اطياف الاشعة فوق البنفسجية - المرئية ، كما تم دراسة اطياف الاشعة تحت الحمراء ( IR ) للمعقدات . وقد بينت دراسة التوصيلية المولارية انعدام الصفة الايونية للمعقدات المذكورة ، وباعتماد على النتائج المستحصلة لهذه المعقدات استطعنا الاستنتاج بان المعقدات الكليتيية اتخذت الشكل الهندسي الثماني السطوح في كل من معقدات الكوبلت (II) والنيكل (II) وكاديوم (II) .

### Introduction

The earliest works on the heterocyclic dyes were concerned with 8-hydroxy quinoline (8-HQ) as a ligand, This compound was used to detect many cations (Akiyama,1954), whereas Cheng and Bray (Cheng,1955) investigated the reactions of 1-(2-pyridylazo)2-naphthol (PAN) with certain metal ions . They recommended this reagent may used as an indicator and the observing that the chelate complex of PAN might be extracted by organic solvents.

Two reviews included all dyes containing a heterocyclic group ortho to the azo group, synthesized from (8-HQ) derivatives, concerning analytical applications of these heterocyclic azo dyestuffs and closely related compounds, was were published (Navratil,1966) and (Anderson,1967). A survey of the azo dyes prepared from 2-amino

thiazole and 3-amino triazole derivatives was done (Hovind,1975). A large number of the derivatives of these two compounds have been investigated for analytical purposes , and have been used as reagents in addition to being interesting complexing agents(Beck,1970;Nuckaya,2001 and Iriepa,1999).Recent papers concerned with a novel benzothiazole and triazole derivatives reported their ability to form a chelate with many metal ions(Casolaro,2000; Salih,1998; Kalil1999 and puvial,1999) .

Although (Davidson1948) reported a colour reaction of Meldrum's acid with sodium nitrite, it was not until 1961 that two groups independently isolated the oxime as an unstable yellow solid(Eistert1961and Zayralv1961).Its reduction over platinum dioxide provides the only known route to the 5-amino compound(Eistert1961),but otherwise the properties of this compound are unknown. Similarly little studied are the hydrazones , prepared by coupling with appropriate diazo compounds(Regitz,1968 and Regitz,1965) or diazonium salts(Eistert1961). The parent 4,5,6-trione of which these compounds are formal derivatives, remains un-prepared, despite a number of attempts(Regitz,1969 and Hochrainer,1966).

The most important nitrogen-containing derivative of Meldrum's acid is the diazo-compound, formed by diazotization of the amine, (Eistert1961) or, more conveniently, by direct reaction with p-toluenesulphonyl azide(Regitz,1968 and Regitz,1965).

## Experimental

### Materials and physical measurements

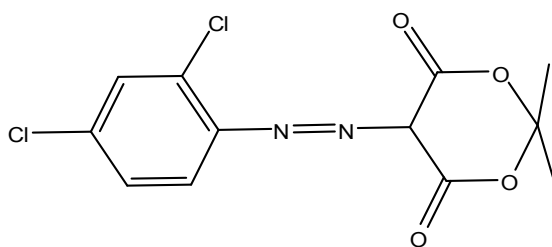
All chemicals used were of highest purity (BDH or Fluka) and used with out further purification.

Absorption spectra were recorded using Shimadzu UV-Vis 1700 spectrophotometer, for solution of the complexes in aqueous ethanol at room temperature. Using 1cm quartz cell. IR spectra were recorded with FT-IR-8000 Shimadzu, in the range of (4000-400)  $\text{cm}^{-1}$  using KBr disc. The magnetic susceptibilities of the complexes were measured on powered samples using the faraday method, for this purpose Balance Magnetic susceptibility model – M.S.B. Auto.Electrical conductivity measured by Digital conductivitymeter Alpha – 800 with solute concentration of  $10^{-3}\text{M}$  in ethanol at room temperature. pH measurements were carried out using ( PH– meter ), 720 , WTW 82362. ,the metal percentages were determined using atomic absorption technique by Shimadzu -AA-160.

### Synthesis and characterization of azo ligand (DPOD)

The ligand prepared by dissolving (0.01 mol) of 2,4-dichloro aniline in 10 ml of distilled water and 5ml of concentrated hydrochloric acid, then the solution was cooled below 5 °C. To this mixture a solution of (0.01 mol) of sodium nitrate in 10 ml of distilled water was added drop wise at 0-5 °C and the mixture was stirred for 15 min. This diazonium solution was added drop wise to a 500 ml beaker containing (0.01 mol) of Meldrum's acid dissolved in 150 ml of alkaline ethanol. The mixture was allowed to stand over night and acidified with dilute hydrochloric acid to pH = 7.0. The crude dyes were collected by filtration and recrystallized from benzene-hexane mixture.

The structural formula of the ligand is shown in figure.1.



Figure(1):- Structure of the ligand 5-((2,4-dichlorophenyl) azo)-2,2-dimethyl-1,3-dioxane-4,6-dione(DPOD)

### Synthesis of complexes

The chelate complexes have been synthesized at optimal pH values dissolved (0.632gm, 0.002 mol) of ligand (DPOD) in 10 ml ethanol and then (0.01 mol) of metal chloride, M= Co(II), Ni(II), or Cd(II) dissolved in 10 ml of buffer solution of ammonium acetate (at optimal pH) is added drop wise with vigorous stirring to the ligand solution. The reaction mixture was left over night then the complexes are filtered off washed with distilled water, then with ethanol and dried in desiccators over anhydrous  $\text{CaCl}_2$ . Table.1 collects the physical properties and analytical data for those complexes are shown in Table 1(Kurtoglu,2010).

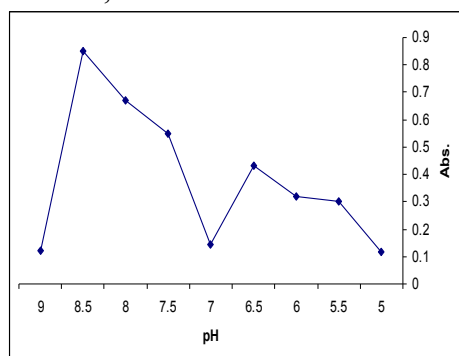
Table(1):- Physical properties of the ligand (DPOD) and its complexes.

No.	Compound	Color	Yield %
1	$\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_4$	Yellow	96.6
2	$[\text{Co}(\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_4)_2]$	Red	78
3	$[\text{Ni}(\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_4)_2]$	Dark green	75
4	$[\text{Cd}(\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_4)_2]$	green	73

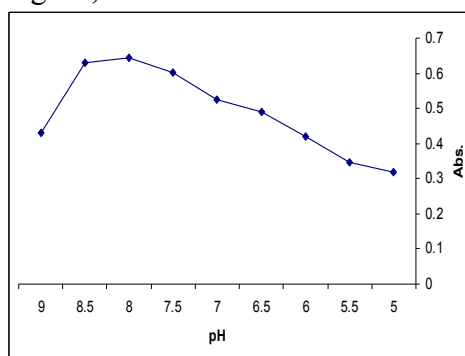
### Results and discussion

#### Effect of pH

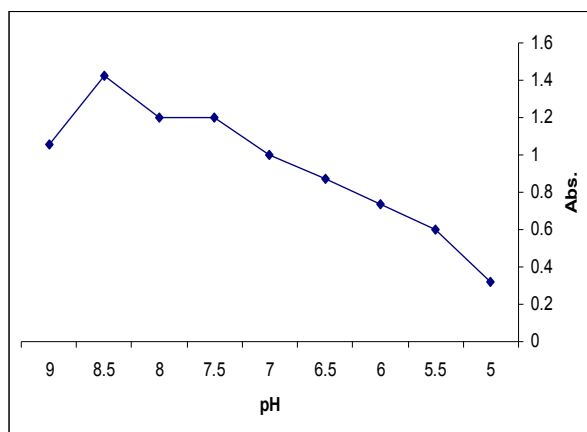
Suitable pH values for metal complex solutions were found to be in the range of (5 – 9). To evaluate the optimal pH values of metal complex solutions by using buffer solution of ammonium acetate The preparation of the complexes has been conducted after fixing the optimum conditions of concentration which obey Lambert-Beers Law these concentration were ( $5 \times 10^{-4}$  -  $9 \times 10^{-4}$ )M. The effect of pH on the absorbance were studied, and the results are shown in Figs. 2, 3 and 4.



Figure(2):-The effect of pH on the absorbance Of metal complexe Co(II) with the ligand(DPOD)at optimal conc. =  $5 \times 10^{-5}$  M



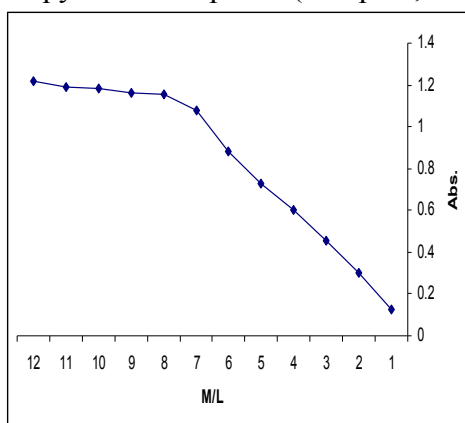
Figure(3):-The effect of pH on the absorbance Of metal complexe Ni(II) with the ligand (DPOD)at optimal conc. =  $5 \times 10^{-5}$  M



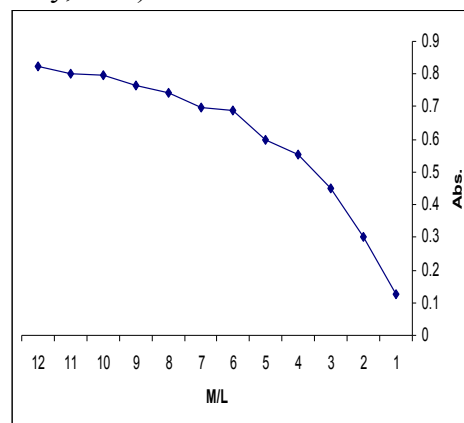
Figure(4):-The effect of pH on the absorbance Of metal complex Cd(II) with the ligand(DPOD)at optimal conc. =  $5 \times 10^{-5}$  M

### Metal: ligand ratios

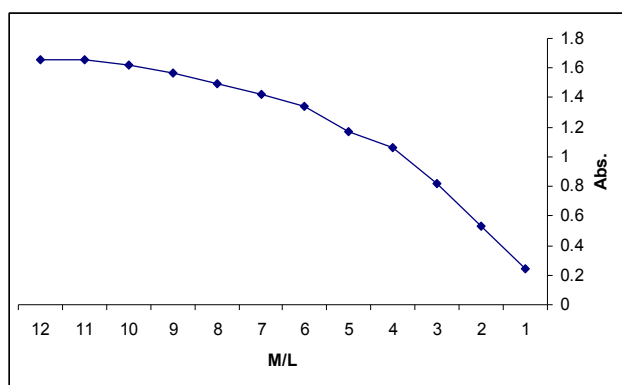
The metal : ligand ratio (M:L)of complexes were determined by the molar ratio method at the wavelength of maximum absorption ( $\lambda_{max}$ )and fixed pH and concentration .The ligand (DPOD)was found to form chelates with all metal ions mention as shown in Figs. 5, 6and 7. The results are in agreement with the values reported for some antipyrilazo complexes(Karipcin,2007and Muheey,2008).



Figure(5):- The molar ratio (M:L) Of metal ion Co(II) with the ligand(DPOD) at optimal conc. =  $5 \times 10^{-5}$  M



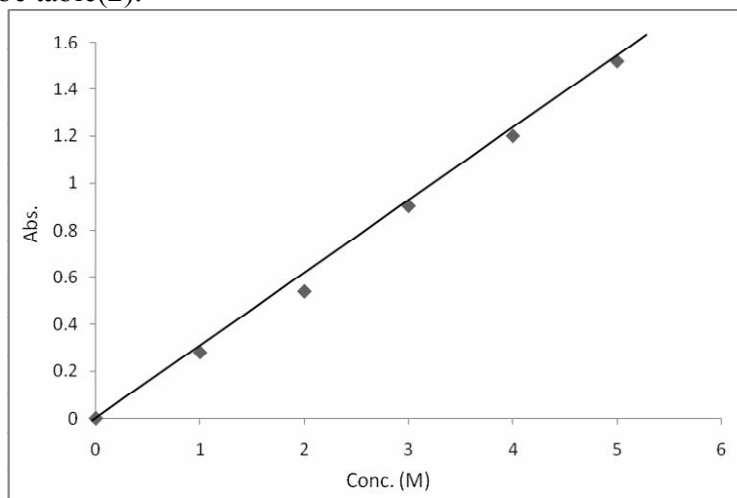
Figure(6):- The molar ratio (M:L) Of metal ion Ni(II) with the ligand(DPOD) at optimal conc. =  $5 \times 10^{-5}$  M



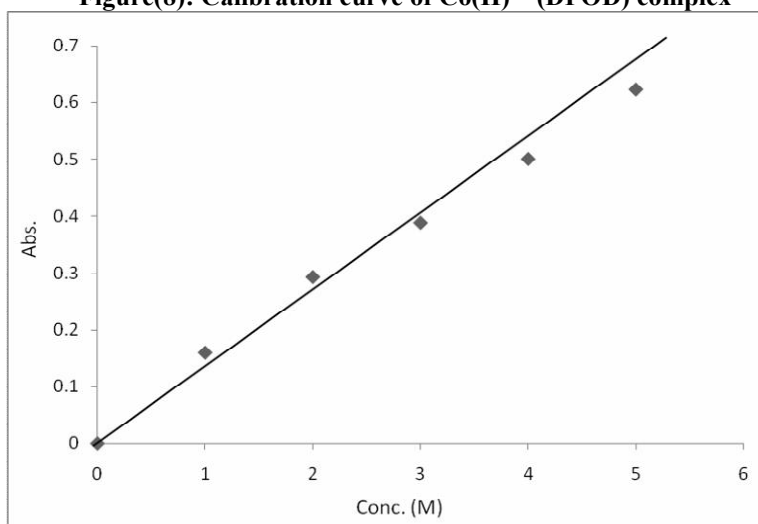
Figure(7):- The molar ratio (M:L) Of metal ion Cd(II) with the ligand(DPOD) at optimal conc. =  $5 \times 10^{-5}$  M

### Calibration curve

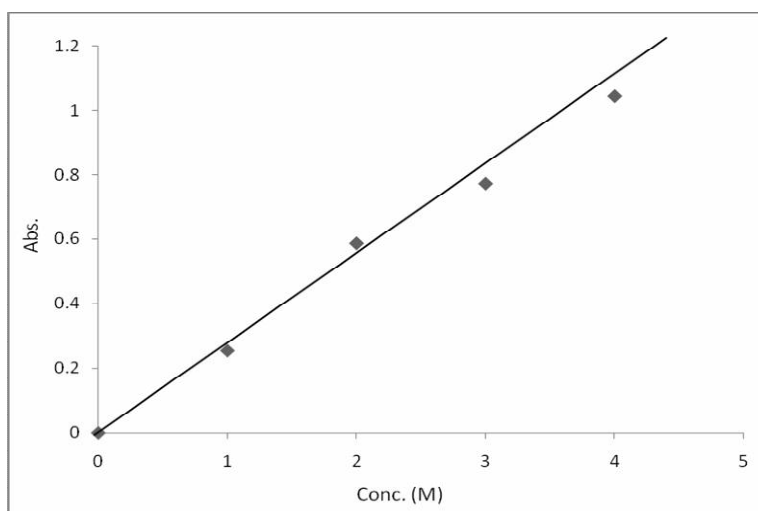
Linear calibration graph through the origin was obtained which obeyed Beers law over the range(1-5) ppm of Co(II), Ni(II), or Cd(II). The average molar absorptivity was found to be table(2).



**Figure(8): Calibration curve of Co(II) – (DPOD) complex**



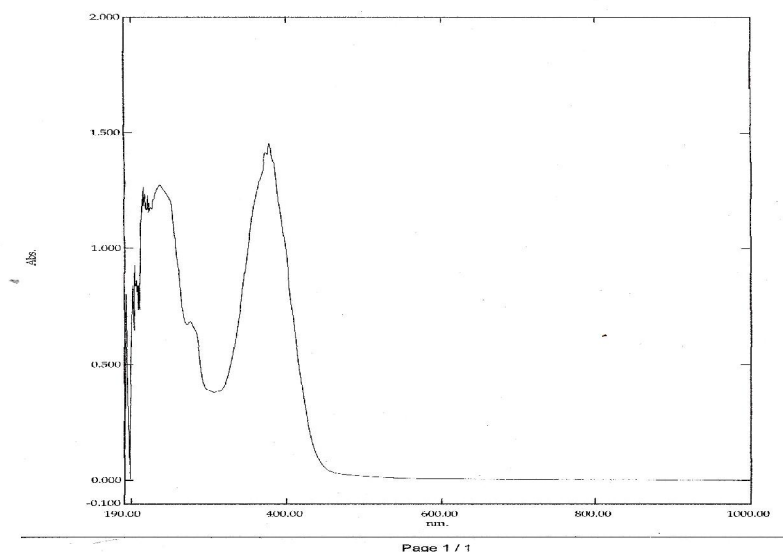
**Figure(9): Calibration curve of Ni(II) – (DPOD) complex**



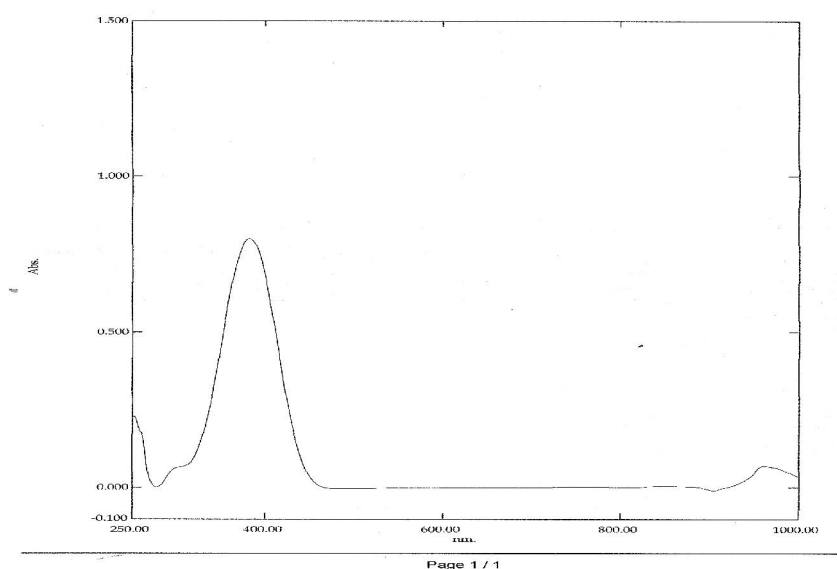
**Figure(10): Calibration curve of Cd(II) – (DPOD) complex**

## Absorption spectra

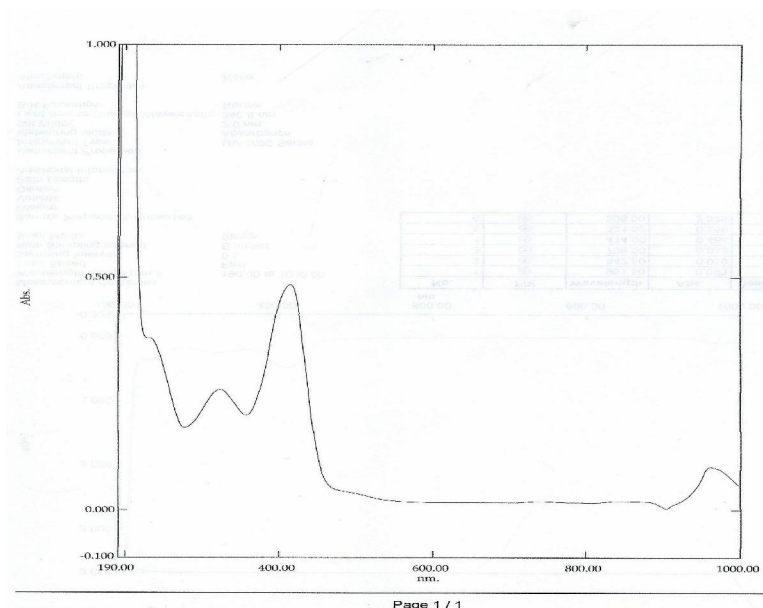
The absorption spectra of ligand (DPOD) and its complexes were studied and shown in figures 8,9,10 and 11. The wavelength for the maximum absorption ( $\lambda_{\max}$ ) of the ligand was found at 378 nm. The spectra of metal complexes were recorded within wavelength range (380– 414) nm. The absorption maxima ( $\lambda_{\max}$ ) of each complex also shown in Table.2. two absorption bands were appear at the free ligand (DPOD) spectrum. The bands at 235 nm referring to the  $\pi \rightarrow \pi^*$  transitions of benzene ring while the band at 378 nm is due to the charge transfer characters.



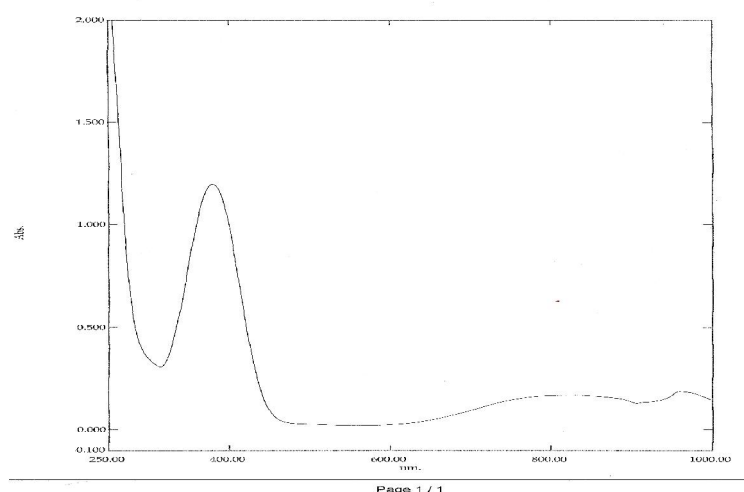
Figure(11):- Absorbance spectra of ligand (DPOD) at  $\lambda_{\max}=378$



Figure(12):- Absorbance spectra of ligand (DPOD) with ion complex of Co(II)  
Conc.  $5 \times 10^{-5}$  M at  $\lambda_{\max}=382$



**Figure(13):- Absorbance spectra of ligand (DPOD) with ion complex of Ni(II)**  
**Conc.  $5 \times 10^{-5}$  M at  $\lambda_{\max} = 414$**



**Figure(14):- Absorbance spectra of ligand (DPOD) with ion complex of Cd(II)**  
**Conc.  $5 \times 10^{-5}$  M at  $\lambda_{\max} = 380$**

**Table(2):- The optimal pH values, optimal molar concentration, wavelength ( $\lambda_{\max}$ ) and molar absorptivity ( $\epsilon$ ) of complexes**

Complex	Optimal pH	Optimal molar conc. (M)	Optimal wave length ( $\lambda_{\max}$ ) nm	Molar absorptivity ( $\epsilon$ ) $\text{L.mol}^{-1}.\text{cm}^{-1}$
$[\text{Co}(\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_4)_2]$	8.5	$5 \times 10^{-5}$	382	30400
$[\text{Ni}(\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_4)_2]$	8	$5 \times 10^{-5}$	414	12440
$[\text{Cd}(\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_4)_2]$	8.5	$5 \times 10^{-5}$	380	27040

### **$^1\text{H}$ -NMR and Infrared spectra**

The  $^1\text{H}$ -NMR spectrum of ligand (DPOD) fig.13,  $\delta$  1.7 ppm (s,6H) for methyl ;  $\delta$  3.3 ppm (s,1H) for methine ;  $\delta$  (6- 6.3) ppm (m,3H) for phenyl.

The infrared spectra of the free ligand (DPOD) and its complexes with Co (II), Ni (II) ) and Cd(II) are given in Table.3. These spectra are complicated owing to the extensive overlap of number of bands arising from  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{N}=\text{N})$  and