

# INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES

(p-ISSN: 2348-5213; e-ISSN: 2348-5221)  
www.ijrcps.com



## Research Article

### SYNTHESIS OF NEW MACROCYCLIC SCHIFF BASELIGANDS AND INVESTIGATION OF THEIR ION EXTRACTION CAPABILITY FROM AQUEOUS MEDIA

HAMID HUSSEIN EISSA

Assistant Professor in Physical organic Chemistry -Chemistry Department, Applied College Sciences,  
University of Hajah, Yemen.

Corresponding Author: Hamedesia2003@yahoo.com

#### Abstract

Three new macrocyclic Schiff bases: (II), (IV) and (VI) containing nitrogen – oxygen donor atoms were synthesized by reaction of intermediate compounds: 1,4-bis(2-formylphenyl)-1,4-dioxabutane (I), 1,4-bis(2-formylphenyl)-1,4,7-trioxaheptane (III) and 1,10-bis(2-formylphenyl)-1,4,7,10-tetraoxadecane (V) with oxydianiline. Identification of these macrocyclic Schiff bases: 1,12-diaza-(3,4;9,10-dibenzo)-13,21-oxydianiline-5,8-dioxacycloheptacosine-1,11-diene (II), 1,15-diaza-(3,4;12,13-dibenzo)-16,24-oxydianiline-5,8,11-trioxacyclo tetraacosine-1,14-diene (IV) and 1,18-diaza-(3,4;15,16-dibenzo)-19,27-oxydianiline-5,8,11,14-tetraoxacyclohepta-cosine -1,17-diene (VI) were determined by LC-MS, IR, <sup>13</sup>C-NMR and <sup>1</sup>H-NMR spectrometry. The liquid-liquid extraction of metal picrates such as Ag<sup>+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> from aqueous phase to organic phase was carried out using these ligands. The effect of chloroform and dichloromethane as organic solvents over the metal picrate extractions was investigated at 25 ± 0.1 °C by using atomic absorption spectrometer. The composition of extracted Ag<sup>+</sup> complex was (2:1) (L:M) and Cu<sup>2+</sup> complex was (1:1) (L:M) for the ligand (VI).

**Keywords:** Macrocyclic schiff bases; Liquid- liquid extraction.

## Introduction

Polyazamacrocycles with large cavities have received recent interests as inorganic cation receptors [1]. The cyclic arrangement of a large number of donor atoms and the flexibility of these ligands make them good hosts for ions [2]. They were also used as spectrophotometric analytical reagents [3]. Metal ions have enormous importance in many biological processes, especially heavy metal ions which are effective enzyme inhibitors exerting toxic effects on living system [4]. Therefore, separation and determination of toxic metal ions such as mercury, lead, and cadmium in environmental sources play an important role for healthy life [5]. Although new paragraph macrocyclic compounds containing oxygen, sulfur, and nitrogen are known. Macrocyclic compounds used in solvent extraction were mostly the oxygen donor type [6]. A number of methods for the preparation of the large polyazamacrocyclics have been reported. The most common synthetic procedure

requires the use of *N*-tosyl groups to protect and activate the nitrogen atoms in the cyclization step [7]. Ring closure occurs by a condensation reaction of *N*-tosylated polyamines with the appropriate ditosylate ester or dihalide in DMF in the presence of base [8]. These reactions allow the production of polyazamacrocycles in moderate yields [9], but removing the *N*-tosyl groups requires drastic conditions and is not always straightforward. Another cyclization process uses the template ring closure for formation of cyclic di- or tetradentate Schiff bases. This is a simple process, but it is often difficult to choose the correct template metal ion or to predict certain ring contraction reactions were the template cation dose not coordinate with all of the ring nitrogen atoms [10]. In some cases, reduction of the cyclic Schiff base and removal of the template ion have been difficult [11]. A non template method for the formation of macrocyclic poly Schiff bases has also been

studied. This procedure often gave a polymeric material beside cyclization reaction, while there is no need to remove a metal ion [12]. In the present work we used a non template method for the formation of four novel macrocyclic Schiff bases: (III) , (IV), (V) and (V) then were used for removed of various metal ions from the aqueous phase into the organic phase in liquid – liquid extraction system.

All the chemicals used were of AnalaR grade and procured from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received. Distilled water was used in the extraction experiments. The solvents were saturated with each other before use in order to prevent volume changes of the phases during extraction. The C, H, and N were analyzed on a Carlo-Erba 1106 elemental analyzer. The IR spectra was recorded on Jusco 300 instrument in KBr pellets. <sup>1</sup>H NMR spectra of ligands in CDCl<sub>3</sub> solution were recorded on a Bruker DT-400 MHz spectrometer, and chemical shifts are indicated in ppm relative to tetra methyl silane. Mass spectra were recorded using a KRATOS MS50TC spectrometer. AA 929 Unicam Spectrometer was used for FAAS measurements with an air-acetylene flame. A pH meter (Metrohm–691pH Meter) was also used. All extraction experiments were performed by using a mechanical flask agitator in 50 cm<sup>3</sup> stoppered glass flasks, M.P Apparatus Digital (32-300 °C).

### Synthesis of , '-bis(2-carboxyaldehyde phenoxy) xylene (II)

To a stirred solution of salicylaldehyde (2.44g , 0.02mol) and K<sub>2</sub>CO<sub>3</sub> (1.38 g , 0.01mol) in DMF (50ml) , '- Dichlor-p-xylene (1.39g , 0.01 mol) in DMF(10ml) was added dropwise. The reaction was heated for 4h at 150-155°C and then stirred at room temperature for 4h, after the reaction was completed, 100 ml distilled water was added, left in a refrigerator for 1h , the precipitate was filtered[2,11], washed by 50 ml water, dried in air and recrystallized from ethanol. (scheme No.2)

### Synthesis 1,16-di aza-3,4,13,14-tri phenyl-17,25 -di phenyl sulphide-5,12-di 2.1.5. Synthesis of 1,16-di aza - 3,4,7,10,13,14-tri phenyl -17,19 – (triazine-6-phenyl) -5,12-di oxacyclo penta-icozane-1,15-diene (V)

The macrocyclic compound (V) was prepared by dropwise addition of a solution of 4-Aminophenyl sulfone (0.374 g, 0.002 mol) in methanol (40 ml) to a stirred solution of compound (I) (0.692g, 0.002 mol) in methanol (60 ml). The stirring was continued for 12h, a white powder[14] was precipitated which was filtered

and washed with cold diethyl ether, and recrystallized from mixed (DMF , ethanol. 9:1). (scheme No.5).

Yield: 75 % , colour: Yellow, m.p> 300 °C dec. formula:(C<sub>31</sub>H<sub>23</sub>N<sub>5</sub>O<sub>2</sub>), M.Wt:(497 g).

IR (KBr disk): 3035.96-3059.10cm<sup>-1</sup>(C-H), aromatic),2897.08-2978.09cm<sup>-1</sup>(C-H), aliphatic),1620.21cm<sup>-1</sup>(C=N),1600.92-1570.06cm<sup>-1</sup>(C=C, aromatic),1280.73cm<sup>-1</sup> (C-O).

<sup>1</sup>H-NMR(CDCl<sub>3</sub>-400MHz) δ = 10.590 (s,2H,CH=N) , 7.069 - 8.269 (m,17 H, Ar) , 5.169-5.244 (s,4H ,O-CH<sub>2</sub>-Ph-),3.408-5.737(Solvent organic).

Elemental analysis found % C : 74.92, H:4.62, N:13.98, O:6.48 calculated for (C<sub>31</sub>H<sub>23</sub>N<sub>5</sub>O<sub>2</sub>) % C: 74.83, H: 4.66 , N: 14.08 , O: 6.43

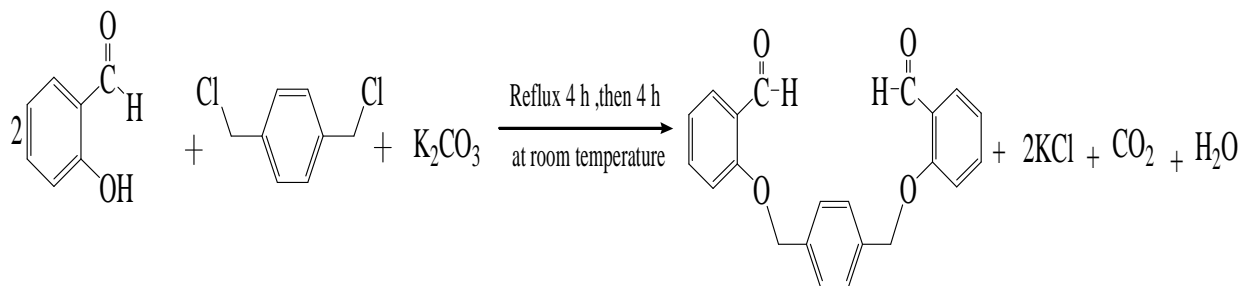
### Procedure of Extraction

The extraction properties of the Schiff base ligand (I) was investigated under liquid–liquid phase and neutral condition using transition metalpicrates Cr(III), Co(II), Cd(II) as substrates and measuring by UV–vis measurements the amounts of metal picrate in the aqueous phase before and after treatment with the compounds. About 10 mm of 2×10<sup>-5</sup> M aqueous picrate solution and 10 mm of 1×10<sup>-3</sup> M solution of ligand in CHCl<sub>3</sub>,CH<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>H<sub>6</sub> were vigorously agitated in a stoppered plastic tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water bath at 25 °C for 1 h, and finally left standing for an additional 30 min. The concentration of the picrate ion remaining in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no picrate extraction occurred in the absence of ligand. Transition metal picrates were prepared by successive addition of a 1×10<sup>-2</sup>M metal nitrate solution to 2×10<sup>-5</sup>M aqueous picric acid solution and shaken at 25 °C for 1 h. These metalpicrates Cr(III), Co(II), Cd(II) were measured by UV–vis using maximum wavelength 352 nm. For each combination of host and metal picrate, the picrate extraction was conducted on three different samples and the average value of percent picrate extracted, with a standard deviation, was calculated. In the absence of host, a blank experiment, no metal ion picrate extraction was detected. The extractability was calculated by using the equation below:

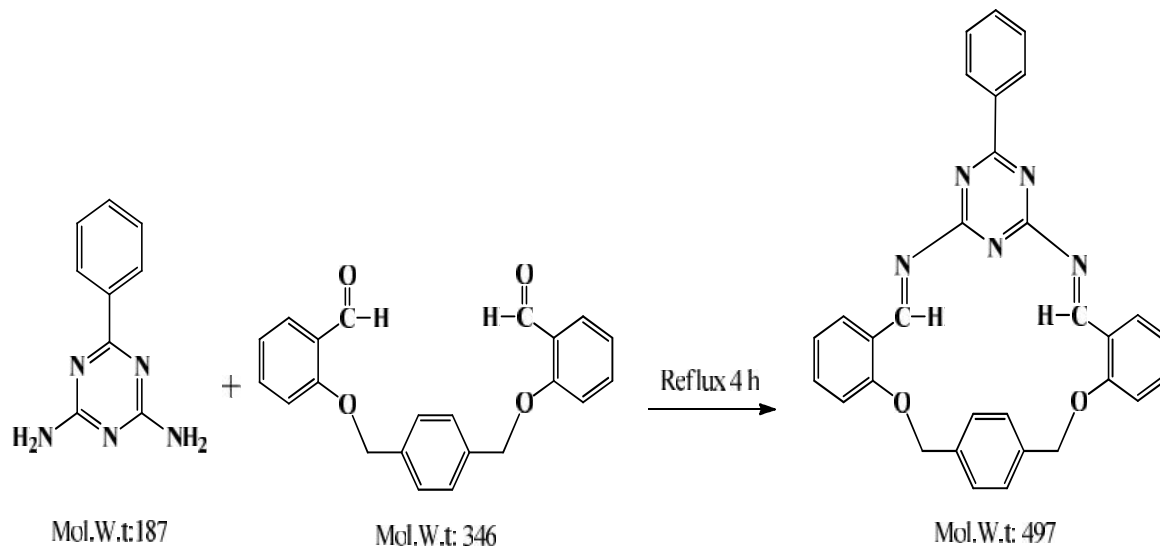
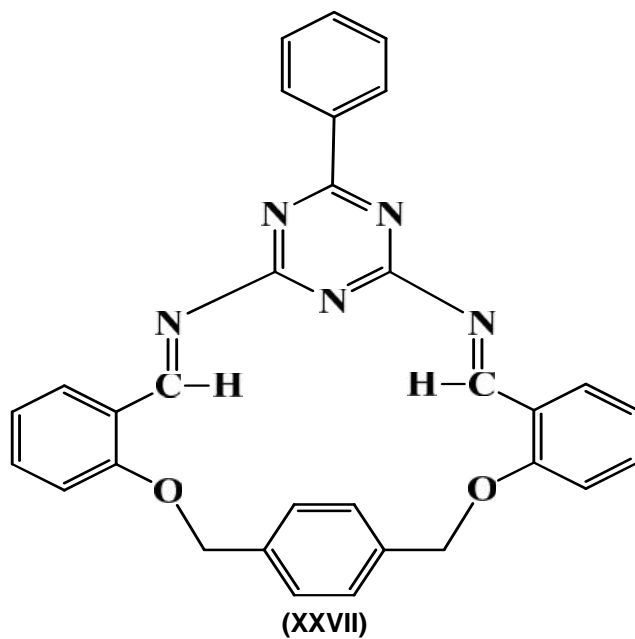
$$\text{Extractability (\%)} = \left( \frac{A_0 - A}{A_0} \right) \times 100$$

where A<sub>0</sub> is the absorbance in the absence of ligand. A denotes the absorbance in the aqueous phase after extraction.[Bülent .D., 2009].

scheme No.2



scheme No.5



## Results and Discussion

### Synthesis

The prepared macrocyclic (III, IV, V, VI) were synthesized by the condensation of by condensation of intermediate compounds 1,6- bis (2- formylphenel) hexane (I) and , 'bis(2-carboxyaldehyde phenoxy) xylene(II) with both 4,4'-Diaminodiphenylmethane and 4-Aminophenyl sulfone in the molar ratio 1:1 in absolute methanol. Also new open Schiff bases(VI) which was prepared by condensation of benzyl hydrazidewith 1,6- bis (2- formylphenel) hexane in the molar ratio 2:1 in DMF. The reactions proceeded smoothly, producing the corresponding Schiff bases ligands in good yield. The ligands are soluble in common organic solvent but insoluble in water. The structures of the ligands were elucidated by elemental analyses, MS, FTIR, electronic absorption, and  $^1\text{H-NMR}$  spectra, which help in elucidating their empirical formula Table 1.

### Elemental analyses of macrocyclic and open (III, IV, V,VI).

The results of elemental analyses macrocyclic and open (III, IV, V, VI), as shown in Table 2, are in good agreement with those required by the proposed formulae.

### IR spectra analysis of macrocyclic Schiff bases(III, IV, V, VI).

**Compound (III)** A strong band at  $1660.4\text{ cm}^{-1}$  in the IR spectrum of the macrocyclic Schiff base (Figure (1)) are assigned to (C=N) of azomethine vibrations. The band in the spectra at  $1593.3 - 1573.7\text{ cm}^{-1}$  is due to (C=C) of aromatic rings. The band in the spectra at  $1243.5\text{ cm}^{-1}$  is due to (C-O) . while the band at  $2946.7 - 2870.6\text{ cm}^{-1}$  is attributed to (C-H aliph). Also, the band at  $3083.3 - 3041.8\text{ cm}^{-1}$  is attributed to (C-H ar).[2,11,14,15].

However, in the IR spectra of Schiff bases this band (C=O) disappears and a new vibration band for azo methane (-HC=N-), indicating that complete condensation takes place.[17-18].

### $^1\text{H-NMR}$ Spectra of macrocyclic Schiff bases (III, IV, V, VI).

**Compound (III):** The  $^1\text{H NMR}$  spectrum (Figure (5)) of the Schiff base (III), showed that in the signals at 8.512

ppm were assigned to the protons of imine -CH=N groups, The multiple signals in the region 1.927 - 1.625 ppm were assigned to protons of methylene groups in two different environments [14,15].The multiple signals in the region 7.766 - 6.954 ppm were assigned to the aromatic protons. While The signals at 4.119 - 4.087 ppm were assigned to the protons of (-O-CH<sub>2</sub>-) group.

The other obtained values for  $^1\text{H-NMR}$  chemical shifts of the compounds are given in the experimental section.[17-18].

The complexation reaction between the ligand (I) and Cr(III), Co(II), Cd(II) ions to produce the ion pair complex have to extracted to the organic phase, this complexationreaction of necessity behave among many optimum condition to reach equilibria and giving stable ionpair complex .

### Effect of pH:

Extracted of 10 ml of Cr(III), Co(II), Cd(II) ions in aqueous phase at different pH (3 –12) by using (10 ml) of ( $1 \times 10^{-4}$  M) ligands dissolved in chloroform, after that shaking the two layers for suitable time and separate this two layers and determined the remainder of Cr(III), Co(II), Cd(II) ions in aqueous phase and Cr(III), Co(II), Cd(II) ions transfer to theorganic phase as complex by stripping method or by difference method according to general procedure, afterward determine the distribution ratio (D) and percentage of extraction (E) at each pH, the results in Table (4), and Fig. (5) shows the optimum of pHextraction was ( $\text{pH}_{\text{ex}} = 7$ ). At pH less than optimum value effect to protonated ligand to Cr(III), Co(II), Cd(II) the pair of electron and then can't coordinate strongly with Cr(III), Co(II), Cd(II) ions and give less stable ion pair complex and minimize the distribution ratio (D) and percentage of extraction (E), also atpH values more than optimum value effect to decrease distribution ratio (D) and percentage ofextraction (E) by reason of formation ion pair complex contain anion (OH<sup>-</sup>) this complex more soluble in aqueous phase and less extracted to organic phase and sovereignty the dissociation equilibria

### Effect of Shaking Time:

Extraction of Cr(III), Co(II), Cd(II) ions from (10 ml) aqueous phase at (pH = 7) by using (10 ml) of organic phase of ( $1 \times 10^{-4}$  M) ligand dissolved in chloroform, after shaking the two phases at different times, separate the two phases and determine the concentration of Cr(III), Co(II), Cd(II) ions remainder in aqueous phase and the concentration of Cr(III), Co(II), Cd(II) ions transfer to organic phase as ion pair

complex by previous spectrophotometric method and then determine distribution ratio (D) and percentage of extraction (E). the results in Table (5) and Fig. (6) demonstrate that the

optimum shaking time was (60 min.) to reach the equilibria of complexation reaction and giving higher distribution ratio (D), the shaking time less than optimum shaking time not allow to reach for equilibria and giving low distribution ratio (D), but at shaking time more than optimum time effect to favor the dissociation step on the complexation and minimize the distribution ratio (D) depend on the kinetic energy of reaction.

### Stoichiometry by Slope Analysis Method

To knowing the more probable structure of Cr(III), Co(II), Cd(II) ion pair complex produced, extracted ( $1 \times 10^{-4}$  M) Cr(III), Co(II), Cd(II) ion from (10 ml) aqueous phase at (pH=7) by using (10 ml) of ligand solution dissolved in chloroform at different concentration ( $2 \times 10^{-5}$  M –  $3 \times 10^{-4}$  M), after shaking the two layer for (60 min.), separate these layers and determine the remainder quantity of Cr(III), Co(II), Cd(II) ions in aqueous phase and transfer quantity of Cr(III), Co(II), Cd(II) ions to organic phase as complex, after that determine distribution ratio (D) and percentage of extraction (E) by previous method (spectrophotometric method). Afterward plot log D against log [Ligand]. The results in Table (6) and Fig. (7) shows from the slope of straight line that the more probable structure of ion pair complex extracted was 1:1(metal : ligand).

### Organic Solvent Effect

Solvent extraction method take care of organic extraction method; according to this concept extracted ( $1 \times 10^{-4}$  M) Cr(III), Co(II), Cd(II) ions in (10 ml) aqueous phase at (pH=7) by (10 ml) organic phase contain ligand dissolved in different organic solvents at concentration of ( $1 \times 10^{-4}$  M), after shaking for (60 min) separate the two layers and determine the remainder Cr(III), Co(II), Cd(II) ions in aqueous phase and Cr(III), Co(II), Cd(II) ions transfer to organic phase as Cr(III), Co(II), Cd(II) complex, according to previous method, afterward calculate the distribution ratio (D) and percentage of extraction (E). the results in Table (7) shows there is not any linear relation between distribution ratio (D) and dielectric for organic solvents used in extraction method of Cr(III), Co(II), Cd(II) ions, Fig(8) as well as this results reflect the effect of organic solvent structure on the extraction method and without any effect for polarity of organic solvent, and reflect the effect on ion pair complex extracted to be

contact ion pair (tight ion pair) or solvent used separated ion pair (loose ion pair)

### Effect of Temperature

Extraction of Cr(III), Co(II), Cd(II) ions in (10 ml) aqueous phase at (pH = 7) by using (10 ml) of ( $1 \times 10^{-4}$  M) ligand dissolved in chloroform at different

temperature (10 – 40°C), after shaking the two layers for optimum time and separate the two layers, determine distribution ratio (D) according to the general procedure. The results in Table (8) and Fig. (9) illustrate the complexation reaction between ligand and Cr(III), Co(II), Cd(II) ions was Endothermic reaction, that is mean the coordination association between ligand and Cr(III), Co(II), Cd(II) ions increase with temperature increasing.

After calculated the thermodynamic data for extraction method to Cr(III), Co(II), Cd(II) ion by using the below relation:

$$K_{ex} = \frac{D}{[M^{n+}]_{aq}[L]_{org}} \quad (4.1)$$

lot log  $K_{ex}$  against  $1/T$  °K and determine the slope of the straight line relation, calculate  $H_{ex}$  as in the relation.

$$\frac{\Delta \log K_{ex}}{\frac{1}{T}} = \frac{-\Delta H}{2.303 R} \quad (4.2)$$

$$\text{Slope} = \frac{-\Delta H}{2.303 R} \quad (4.3)$$

$$G_{ext} = -RT \ln K_{ext} \quad (4.4)$$

$$(4.5) \quad G_{ext} = H_{ext} - T S_{ex}$$

After application of these relation, found the value of enthalpy for extraction of Cr(III), Co(II), Cd(II) ions were ( $H_{ex} = 103.97, 57.79, 52.14 \text{ kJmol}^{-1}$ ) and Gibbs free energy was ( $G_{ex} = -86.53, -47.76, -46.28 \text{ kJmol}^{-1}$ ) respectively, as well as the entropy was ( $S_{ex} = 608.63, 337.86, 314.44 \text{ JK}^{-1}\text{mol}^{-1}$ ) these results shows from the value of  $H_{ex}$  the ion pair complexes structure was 1 : 1 which is giving low value for  $H_{ex}$ , but the high value for  $S_{ex}$  reflect that complexation reaction was entropic in region [[Arifien, et al., 2003](#)] from other hand the endothermic reaction shows good association between Cr(III), Co(II), Cd(II) ions and ligand and may be produce contact ion pair (Tight ion pair).

**Table 1.** Physical and chemical properties of the synthesized compounds[III]-[VI]

Schiff base	Color	M.Wt	Melting point °C	Yield %	Crystallization Solvent
III	Brown	497	300 <	% 75	DMF , EtOH (9:1)

**Table 2.** Elemental analysis data of the synthesized compounds[III]-[VI].

Schiff base	Elemental analysis Calculated (Found %)				
	C	H	N	S	O
III	74.92 (74.83)	4.62 (4.66)	13.98 (14.08)	-----	6.48 (6.43)

**Table 3.** IR spectral data of the synthesized compounds[III]-[VI].

Schiff base	v(C-O)	v(C=C)	v(HC=N)	v(C-H) aliph	v(C-H) arom
III	1280.73	1600.92- 1570.06	1620.21	2978.09 - 2897.08	3059.1 - 3035.96

**Table 4.** <sup>1</sup>H-NMR Spectra of the synthesized compounds[III]-[VI]

Schiff	Chemical Shifts ppm		
	C-H aromatic	CH=N	-O-CH <sub>2</sub> -
III	7.904 - 7.069 (m,17 H)	8.269 - 8.250 (d,2H)	5.244 - 5.169 (s,4H)

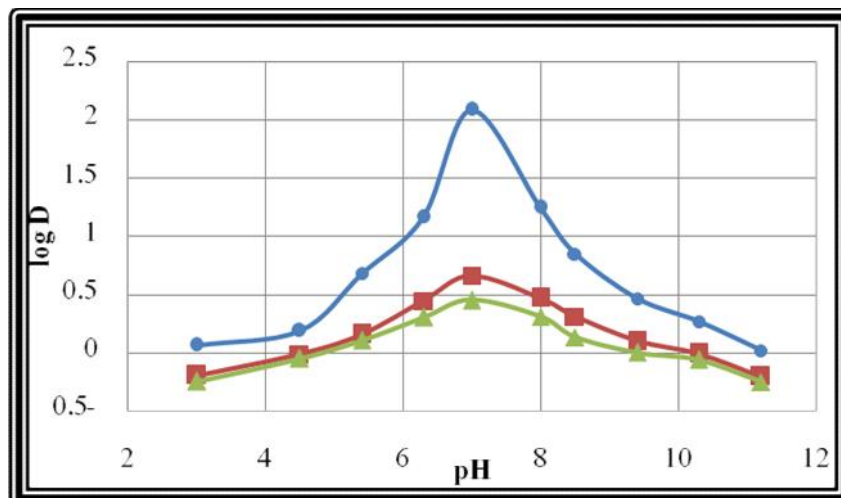
**Fig. (5):** pH effect on the extraction of Cr(III), Co(II), Cd(II) ions

Table (4): Effect of pH on the extraction of Cr(III), Co(II), Cd(II) ions

pH	Cd <sup>+2</sup>			Co <sup>+2</sup>			Cr <sup>+3</sup>		
	log D	D	E%	log D	D	E%	Log D	D	E%
3	-0.237	0.579	36.9	-0.188	0.648	39.3	0.072	1.179	54.1
4.5	-0.043	0.905	47.5	-0.007	0.984	49.6	0.198	1.577	61.2
5.4	0.115	1.304	56.6	0.164	1.457	59.3	0.686	4.848	82.9
6.3	0.309	2.039	67.1	0.451	2.825	72.5	1.173	14.89	92.2
7	0.459	2.876	74.2	0.670	4.682	82.4	2.093	124	99.2
8	0.317	2.075	68.47	0.479	3.013	75.8	1.252	17.87	93.7
8.5	0.139	1.377	60.2	0.318	2.079	62.3	0.856	7.178	841.2
9.4	0.009	1.021	54.5	0.106	1.276	53.8	0.470	2.953	74.7
10.3	-0.051	0.889	46.9	-0.023	0.948	48.7	0.273	1.874	65.2
11.2	-0.246	0.568	37.3	-0.196	0.637	38.9	0.026	1.062	51.5

Table (5): Effect of shaking time on extraction of Cr(III), Co(II), Cd(II) ions

Shaking Time	Cd(II)			Co(II)			Cr(III)		
	Log D	D	E%	Log D	D	E%	Log D	D	E%
10	-0.401	0.397	28.41	-0.329	0.468	31.9	-0.031	0.931	48.2
20	-0.201	0.629	38.6	-0.117	0.764	43.3	0.080	1.203	54.6
30	-0.144	0.718	41.8	0.031	1.075	51.8	0.209	1.62	61.8
40	-0.005	0.988	49.7	0.151	1.416	58.6	0.545	3.505	77.8
50	0.167	1.469	59.5	0.356	2.268	69.4	0.841	6.937	87.4
60	0.345	2.215	68.9	0.527	3.367	77.1	1.669	46.619	97.9
70	0.225	1.68	61.7	0.359	2.289	69.6	1.167	14.673	93.7
80	0.136	1.369	57.8	0.202	1.591	61.4	0.743	5.536	84.7
90	-0.028	0.938	48.39	0.101	1.262	55.8	0.515	3.274	76.6
100	-0.138	0.728	42.12	-0.007	0.984	49.6	0.316	2.068	67.4
110	-0.215	0.610	37.9	-0.131	0.739	42.5	0.159	1.445	59.1
120	-0.386	0.411	29.67	-0.286	0.518	34.1	-0.043	0.905	47.5

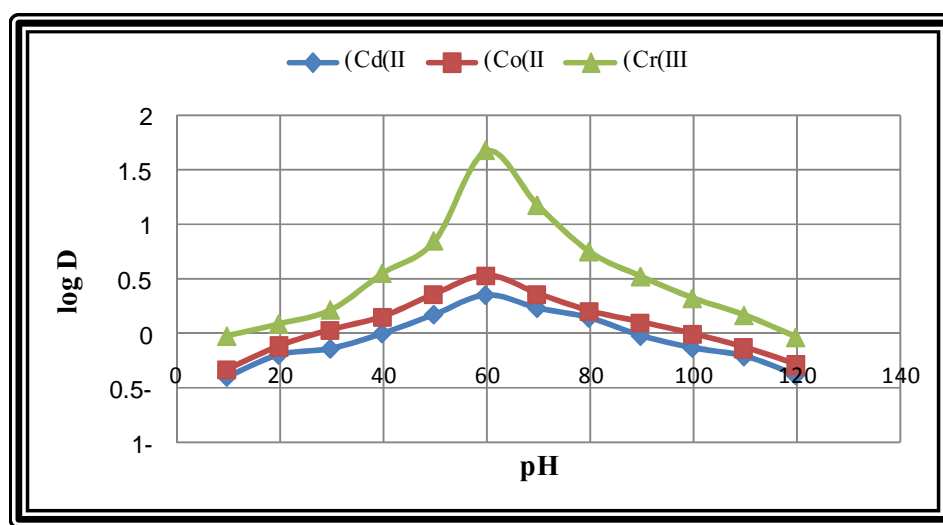
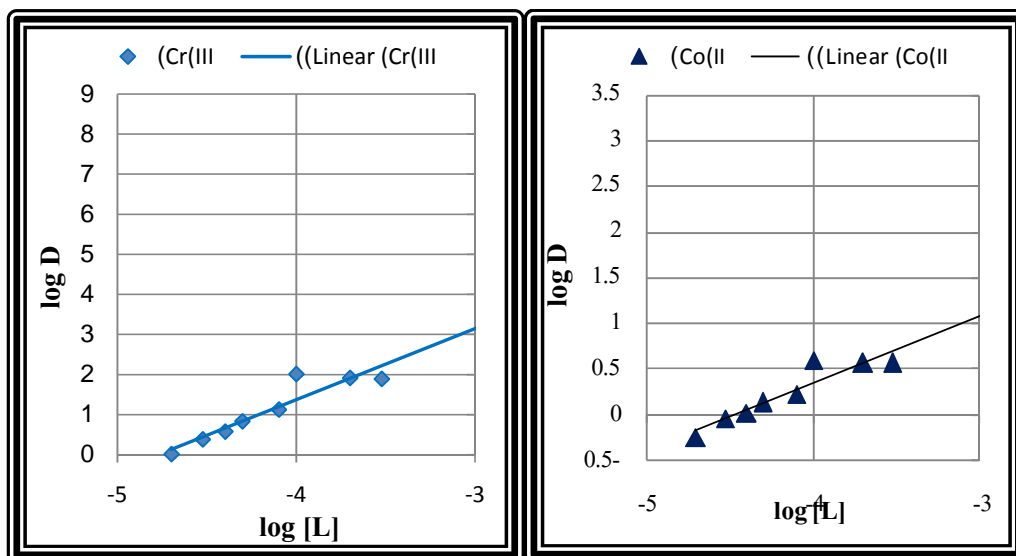


Fig. (6): Effect of shaking time on the extraction of Cr(III), Co(II), Cd(II) ions

**Table (6):** Slope analysis method for extraction of Cr(III), Co(II), Cd(II) ions

Log [L]	Cd(II)				Co(II)				Cr(III)			
	Log D	D	E%	slope	Log D	D	E%	slope	Log D	D	E%	slope
-4.698	-0.487	0.326	17.6	0.66	-0.244	0.570	36.3	0.731	0.01	1.023	50.57	1.385
-4.522	-0.319	0.479	28.7		-0.039	.914	47.8		0.38	2.399	70	
-4.397	-0.215	0.609	37.4		0.021	1.05	51.2		0.573	3.74	78.9	
-4.301	-0.178	0.664	51.5		0.132	1.35	57.4		0.833	6.81	87.2	
-4.097	0.023	1.054	57.4		0.228	1.69	62.8		1.123	13.274	92.2	
-4	0.23	1.698	62.9		0.596	3.95	79.8		2.01	102.33	99.03	
-3.698	0.225	1.679	62.2		0.564	3.66	78.5		1.912	81.66	98.8	
-3.522	0.219	1.656	60.7		0.569	3.71	78.8		1.89	77.625	98.7	



**Fig. (7):** Slope analysis method for extraction of Cr(III),Co(II) ions



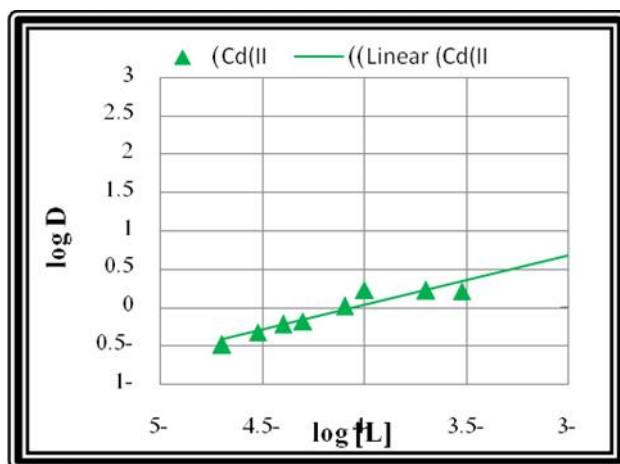


Fig. (8): Slope analysis method for extraction of Cd(II) ions

.Table (7): Organic solvents effect on the extraction of Cr(III), Co(II), Cd(II) ions

Solvents		Cd(II)			Co(II)			Cr(III)		
		Log (D)	D	E %	Log (D)	D	E %	Log (D)	D	E %
Dichloro methane	9.08	0.002	1.004	50.1	0.605	4.025	80.1	1.03	10.63	91.4
Chloroform	5.708	0.393	2.472	71.2	0.12	1.31	56.7	1.95	89.9	98.9
Benzene	2.804	-0.294	0.508	33.7	0.38	2.37	70.3	0.62	4.18	80.7

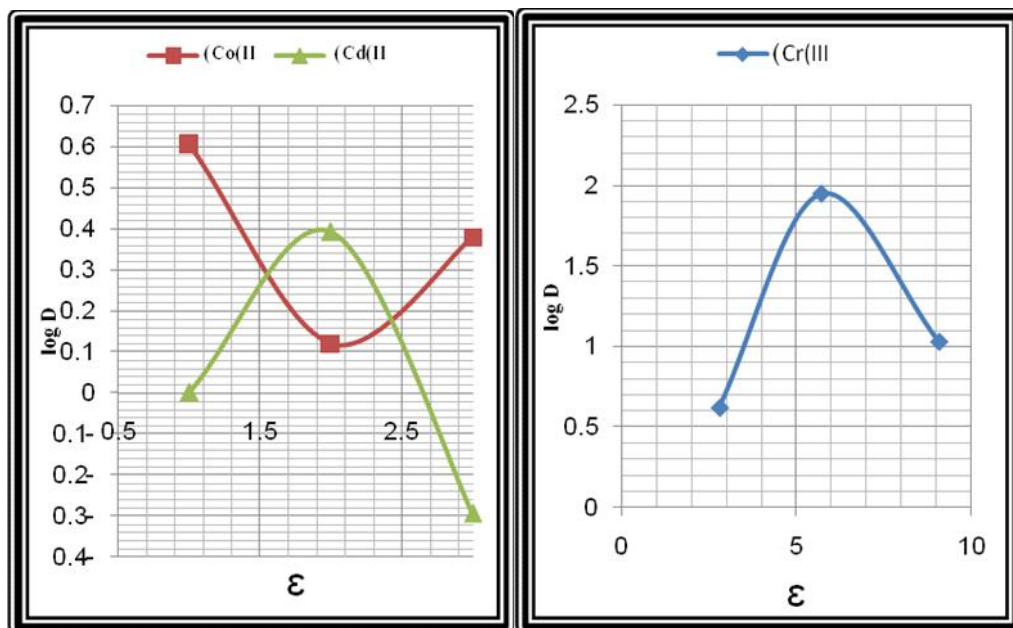


Fig. (8): Effect of solvents organic on the extraction of Cr(III), Co(II), Cd(II) ions

**Table (8):** Temperature effect on the extraction of Cr(III), Co(II), Cd(II) ions

T.C °	T.K <sup>0</sup>	1/Tx10 <sup>-3</sup> K <sup>0</sup>	Cd(II)			Co(II)			Cr(III)		
			Log (D)	D	E %	Log (D)	D	E %	Log (D)	D	E %
10	283	3.5	0.014	1.033	45.6	0.079	1.19	55.8	0.624	4.21	80.82
20	293	3.4	0.22	1.681	62.7	0.378	2.39	67.5	1.29	19.5	95.12
30	303	3.3	0.57	3.75	78.93	0.632	4.29	80.4	1.88	75.92	98.7
40	313	3.2	0.83	6.78	87.2	0.984	9.64	90.6	2.522	165.7	99.4

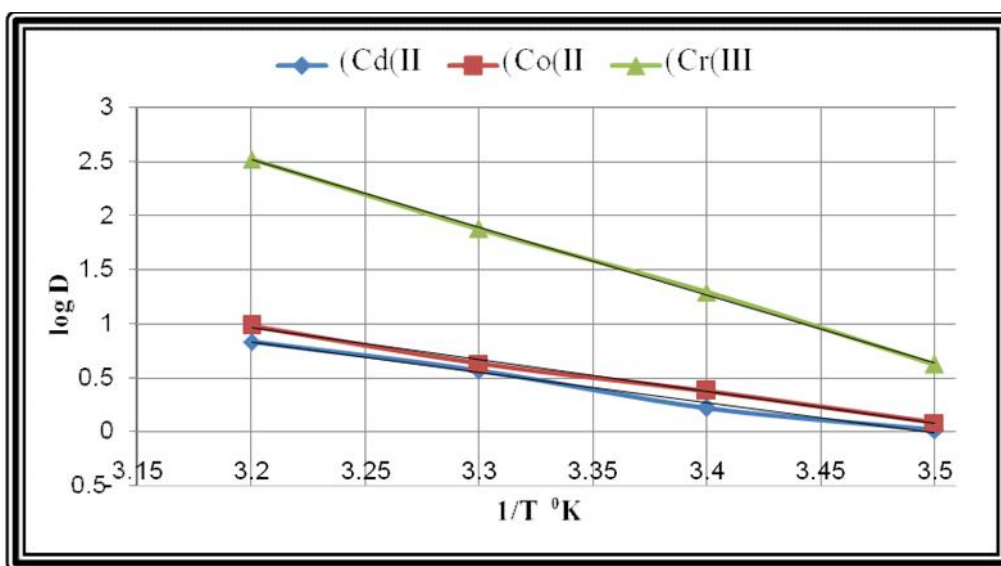


Fig. (9): Temperature effect on the extraction of Cr(III), Co(II), Cd(II) ions

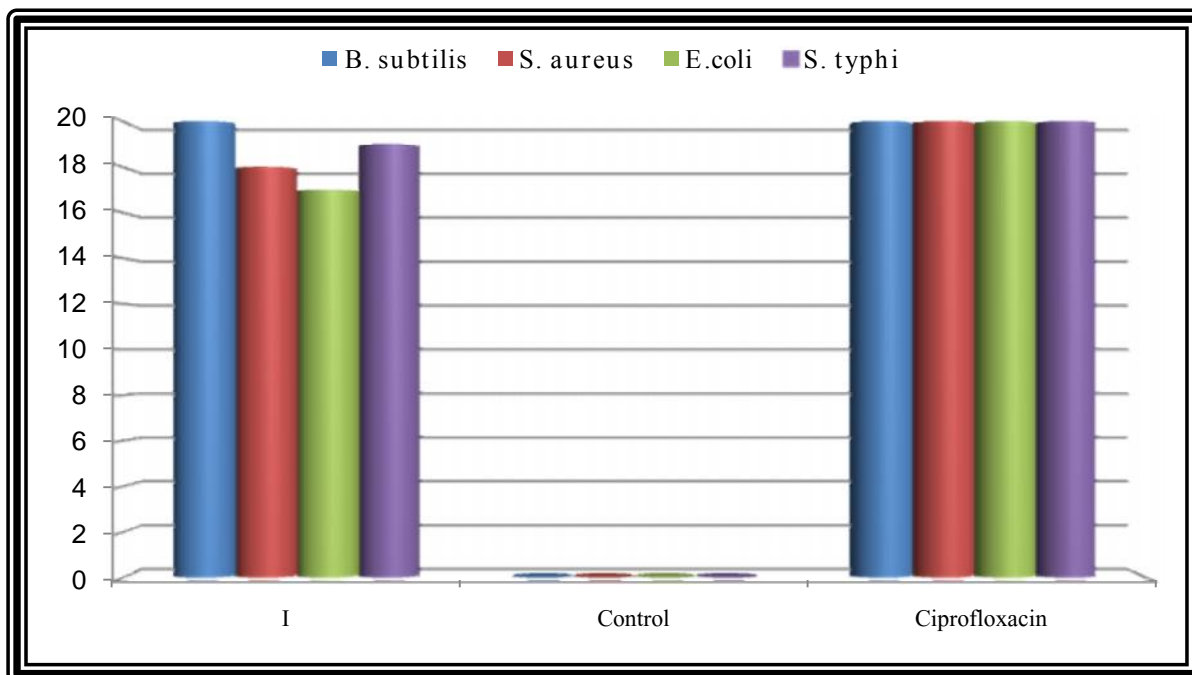
Table (8): Thermodynamic parameters of Cr(III), Co(II), Cd(II)ions

Cation	K <sub>ext</sub>	S <sub>ext</sub> jK <sup>-1</sup> mol <sup>-1</sup>	G <sub>ext</sub> kJmol <sup>-1</sup>	H <sub>ext</sub> kJmol <sup>-1</sup>
Cr(III)	276.1 x 10 <sup>12</sup>	608.63	-86.53	103.97
CO(II)	10.26x 10 <sup>7</sup>	337.86	-47.99	57.76
Cd(II)	52.9 x 10 <sup>6</sup>	314.44	-46.28	52.14

**Table 5.** Antibacterial activity of the synthesized compounds[VI]-[IX]

Shiff base	Bacteria			
	Gram negative		Gram positive	
	B. subtilis	S. aureus	E.coli	S. typhi
I	20 mm	18 mm	17 mm	19 mm
Control	00 mm	00 mm	00 mm	00 mm
Ciprofloxacin	20 mm	20 mm	20 mm	20 mm

(-)No zones of inhibition were observed.  
 Moderately sensitive,(+)Inhibition zones of 7-10mm.  
 Sensitive,(++)Inhibition zones of 11-14mm.  
 High sensitive,(+++Inhibition zones of 15-20mm



**Figure 13.** Antibacterial activity of synthesized compounds[IV].

### Biological Activity

During the last two or three decades, attention has been increasingly paid to the synthesis of Schiff bases which exhibits various biological activities including antibacterial, fungicidal, tuberculostatic and plant growth regulative properties [41]. It was judicious to investigate the synthesis of various new types of Schiff base and studied their antibacterial activity against four strains of bacteria (Bacillus subtilis, Escherichia coli, Staphylococcus aureus, Salmonella typhi). The concentrations used for the screened compounds are 50, 100, and 200 µg/ml. Ciprofloxacin was used as

reference standard while DMSO as control and inhibition zones are measured in mm. The new compounds were tested against one strain each of a gram positive and two gram negative. The test results presence in Table (3.11), a new compound was active against tested and another compounds are no active.

All compounds are no active where used 50, 100 µg/ml but active in the concentrations 200 µg/ml see table (3.4).

### Conclusion

1- The (IV) compound is new and was prepared for the first time.

2- The new compound was identified by <sup>1</sup>HNMR, IR, LC-MS spectral methods.

3- The compound showed a high draw ratio of copper ion at pH = 5.2 and the best organic stores is chloroform and that there is no linear relationship between the polarity of the shops and the distribution ratio(D).

4- That shaking a time more than a time best, which represents the time required to complete the process complexity and give a complex stable lead to lower values ratios distribution D and this would lead to the possibility of a reflection of interaction and increase the speed of interaction back and eventually dismantle the complex and perhaps a few Side reactions that maylead to the occurrence of the phenomenon of the three layers (Three layers) for the analysis of solutions and this is what requires us to comply with a time of shaking out the best

5- That the rate of ion correlation between copper and composite studied by Molar (cation: connected (1:1) between the ligand and the cation.

6- Calculated some parameters associated with extraction, such as constant extraction as well as parameters thermodynamic namely, enthalpy change (  $H^*$ ), entropy change (  $S^*$ ), and Gibbs free energy change (  $G^*$ ).

7-proven data study the effect of different temperatures on the recovery operations that the formation of complexes between ligand and cation studied endothermic (Endothermic) , as indicated negative values of energy free to spontaneous reactions, as also indicated positive values of entropy system that many random.

8-The prepared compound has been biologically screened i.e. studying their effects against two gram-

positive, two gram-negative bacteria. The results show that their activities were found to vary from moderate to very strong.

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