

INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES

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



Research Article

EXTRACTION OF Cr(III), Co(II), Cd(II) IONS AND DETERMINATION OF KINETIC PARAMETERS FOR AZO-SCHIFF BASES DEPENDENT ON EXTRACTION TECHNIQUE

Hamid Hussein Eissa

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

Corresponding Author: Hamedesia2003@yahoo.com

Abstract

This work was focused on the prepared of tetradentate Azo-Schiff base which were prepared by condensation of 3-formyl-4-hydroxy phenylazo benzene with Pyridine-2,6-Dicarbohydrazide has been characterized by elemental analyses and IR, mass, ^1H NMR, and ^{13}C NMR spectral data. Azo-Schiff base has been studied by liquid-liquid extraction towards the metal ions [Cr(III), Co(II), Cd(II)] from aqueous phase to organic phase. behave as good extractant ligand for Cr(III), Co(II), Cd(II) ions from aqueous solution, and the study of condition of extraction shows that the optimum pH values for extraction was (pH=7), in addition the optimum shaking time to reach the equilibria was (60 min.), as well as the stoichiometric study by using Slope Analysis Method shows the structure of Cr(III), Co(II), Cd(II) ions complexes with ligand was 1 : 1 (metal : ligand), in addition the study of organic solvent effect appear there is no straight line relation between the distribution ratio for extraction of Cr(III), Co(II), Cd(II) ions and dielectric constant for organic solvents but this study demonstrate there is an effect for the structure of organic solvent used. Calculated some parameters associated with extraction, such as constant extraction (K_{ex}), as well as parameters thermodynamic namely, enthalpy change (ΔH^*), entropy change (ΔS^*), and Gibbs free energy change (ΔG^*) were calculated, and shows the complexation reaction an endothermic.

Keywords: Pyridine-2,6-Dicarbohydrazide, liquid-liquid extraction, stoichiometric, thermodynamic parameters.

Introduction

Azo dyes constitute one of the largest and most varied groups of synthetic organic dyes in use today [Zollinger., 1991]. Azo compounds are highly important, well known and widely used substances in the textile, paper, coloring agents for foods and cosmetics industries. Other application include merging technologies like liquid crystals, organic photoconductors and non-linear optics [Hamon et al., 2009], [Gordon., 1990]. Azo compounds serve as important analytical tools by providing a strongly chromophoric label, the concentration of which is easily determined by colorimetric, spectrophotometric or spectrofluorimetric methods. Besides, azo compounds are important analytical aid compounds serving as pH indicators, complexometric indicators and to a lesser extent, pre-concentration reagents [Patai., 1997]. The pharmacological use of azo

compounds originates from the discovery of the antibacterial action of Prontosil on streptococcal infection by Dogmagk [Carey., 2000]. Furthermore, azo compounds were reported to show a variety of biological activities including antibacterial [Pathak., 2000], antifungal [Xu, & Zeng., 2010], pesticidal, [Samadhiya & Halve., 2001] antiviral [Tonelli et al., 2009] and anti-inflammatory [Rani et al., 2004] activities. Recently heterocyclic azo compounds have been used in the Mitsunobu reaction [Iranpoor et al., 2008]. Usually, azo compounds were synthesized by diazotization of the amine in mineral acid at about 0 °C [Antonov et al., 2010], [Yildiz & Boztepe., 2002]. Solvent extraction of metal chelate complexes has been recognized as an excellent separation method for a long time because of its simplicity, speed, and its wide scope of application.

As solvent extraction does not involve co-precipitation, which is such an undesirable feature of separation based on precipitation, it is frequently appears to be the ideal method for separating trace constituents from large amounts of other substances (Stray, 1964). It has been used in the laboratory and on industrial scale, because of the selectivity of this process in removing a solute from a liquid mixture by a solvent. As a separation technique, it is a partitioning process based on unequal distribution of the solute (A) between two immiscible solvents at equilibrium (US Environmental Protection Agency (EPA), 2004). The process is often very selective and the isolation of the metal in aqueous can usually be made as complete as desired by carrying out successive extraction procedures (Stray, 1964).

Experimental

Reagents and Apparatus.

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

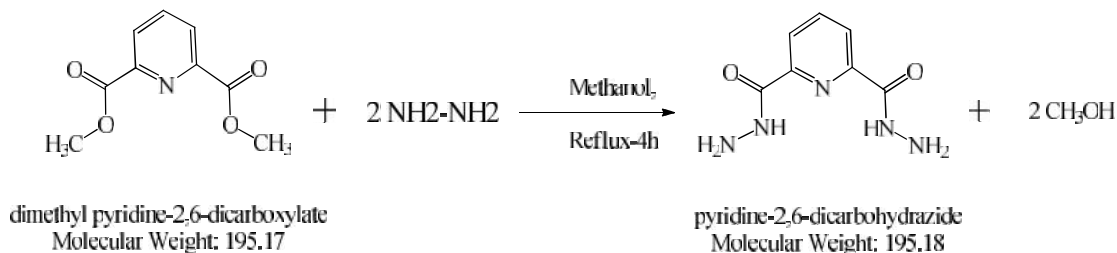
analyzed on a Carlo-Erba 1106 elemental analyzer. The IR spectra was recorded on Jusco 300 instrument in KBr pellets. ¹H and ¹³C-NMR spectra of ligands in CDCl₃ solution were recorded on a Bruker DT-400 MHz spectrometer, and chemical shifts are indicated in ppm relative to tetramethylsilane. Mass spectra 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 cm³ stoppered glass flasks.

Synthesis of Pyridine-2,6-Dicarbohydrazide.

A mixture of dimethyl Pyridine-2,6-dicarboxylate (1.95 g) and hydrazine hydrate (98% 2 cc) in methanol was refluxed for 4-5h. The reaction mixture was allowed to cool to room temperature then, the cooled solution was poured on to ice cold water. The Pyridine -2,6-Dicarbohydrazide thus obtained was filtered and recrystallized from ethanol [Lakshmi et al., 2012].

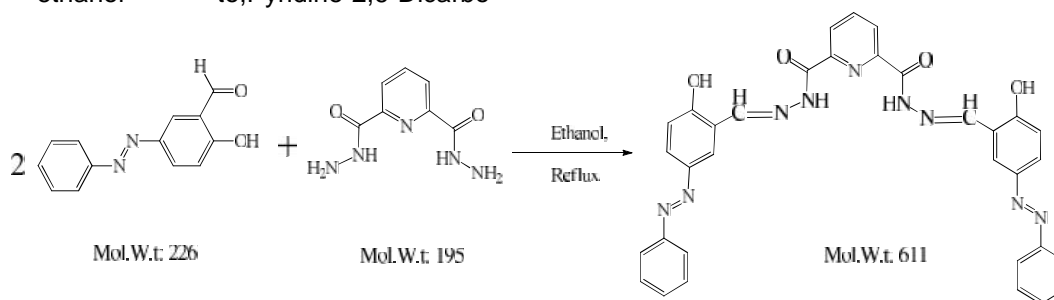
Yield: (87%), m.p. > 280 °C, Empirical formula: (C₇H₉N₅O₂), M.Wt: (195 g).



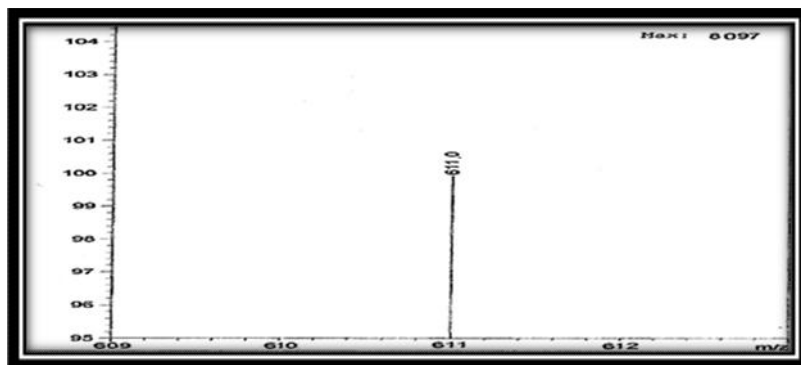
General Method for Synthesis of Azo Schiff bases(I)

Azo-coupled precursors were prepared as described previously [Khanmohammadi & Darvishpour, 2009], [Dinçaple et al., 2007] was added (0.01 mol) of 3-formyl-4-hydroxy phenylazo benzene in 30 ml from absolute ethanol to, Pyridine-2,6-Dicarbo

hydrazide, (0.005 mol) in 60 ml ethanol, The reaction mixture was refluxed for 4 h with continue stirrer. A solid mass formatted on hot. The reaction mixture was allowed to cool room temperature, dark yellow precipitated were filtered and recrystallized from mixture (DMF, Ethanol) (1:9), then dried in vacuum [Salih, & Hamid., 2008 Hamid., 2013].

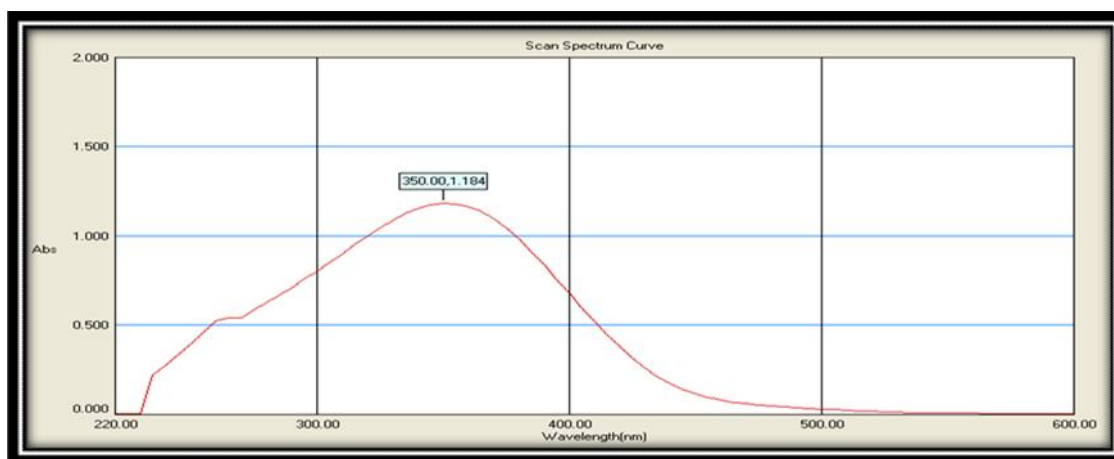


Dark yellow; Yield 89%;
M.Wt : 610 g .(Figure 1)



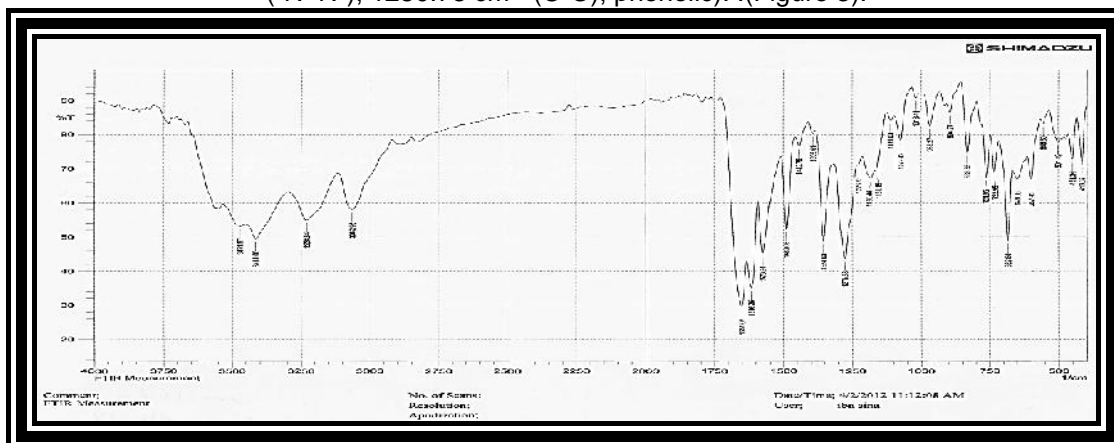
Figure(1) MS spectra of ligand(I)

UV-Vis: λ_{max} = 350 nm.(Figure 2)



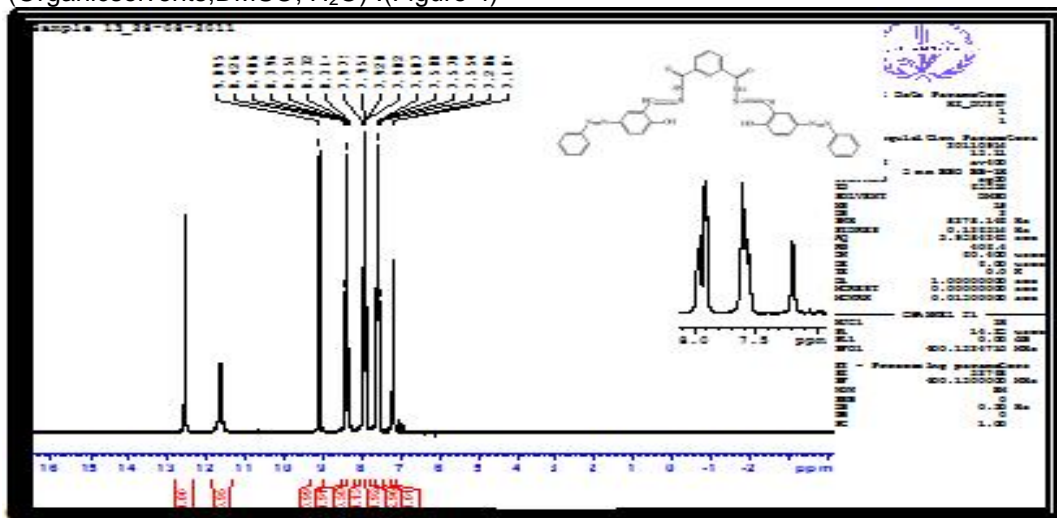
Figure(2) λ_{max} of ligand(I)

IR (KBr disk): 3414.00 - 3471.87 cm^{-1} (O-H), 3228.84 cm^{-1} (N-H, amid), 3062.96 cm^{-1} (C-H), aromatic), 1651.07 cm^{-1} (C=O), 1616.35 cm^{-1} (C=N), 1573.91 cm^{-1} (C=C, aromatic), 1442.75 – 1489.05 cm^{-1} (-N=N-), 1280.73 cm^{-1} (C-O, phenolic). (Figure 3).



Figure(3) IR spectra of ligand(I)

$^1\text{H-NMR}$ (CDCl_3 -400MHz) δ =12.558 (s,2H,OH), 11.642(s,2H,N-H), 9.095 (s,2H,CH=N), 7.184 -8.426 (m,19 H, Ar), 2.259 - 3.338 (Organicsolvents,DMSO, H_2O) .(Figure 4)



Figure(4) $^1\text{H-NMR}$ spectra of ligand(I)

Elemental analysis: $\text{C}_{33}\text{H}_{25}\text{N}_9\text{O}_4$, CaCr(III) , Co(II) , Cd(II) lated (%):C: 64.80; H: 4.12; N: 20.61; O: 10.46.; Found(%):C:64.81, H:4.17, N:20.73, O:10.29.[Hamid.,2013]

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^{-5} M aqueous picrate solution and 10 mm of 1×10^{-3} M solution of ligand in CHCl_3 , CH_2Cl_2 , C_6H_6 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^{-2} M metal nitrate solution to 2×10^{-5} M aqueous picric acid solution and shaken at 25°C for 1 h. These metal picrates 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_0 is the absorbance in the absence of ligand. A denotes the absorbance in the aqueous phase after extraction.[Bülent .D., 2009].

3.1. Result and Discussion

The prepared organic compound (I) was soluble in DMF, DMSO and partially soluble in acetone, Dichloro methane, Benzene, Methyl iso butyl ketone, chloroform, Dimethyl formamide. The compound is characterized by GC-MS, LC-MS, IR, $^1\text{H-NMR}$ spectra, which help in elucidating their empirical formula (Tables 1,2,3)[Hamid.,2013].

Table 1: Color, molecular weight, melting point and Elemental Analysis of (I)

Ligand	Elemental Analysis Found (Collated %)				max nm	Color	Yield %	M.Wt	Melting point $^\circ\text{C}^0$
	C	H	N	O					
I	66.94 (66.88)	4.19 (4.29)	18.40 (18.35)	10.47 (10.48)	335	Dark Yellow	% 80	610	300 <

Table(2) IR Spectra of Ligand (I)

Ligand	$\nu(\text{C-O})$ Cm^{-1}	$\nu(\text{N=N})$ Cm^{-1}	$\nu(\text{C=C})$ Cm^{-1}	$\nu(\text{C=N})$ Cm^{-1}	$\nu(\text{C-H})$ aliph.	$\nu(\text{C-H})$ arom. Cm^{-1}	$\nu(\text{OH})$ Cm^{-1}
I	1280.73	1442.75 – 1519.91	1573.91	1616.35	-----	3051.39	3414.00 - 3479.58

Table(3) $^1\text{H-NMR}$ Spectra of Ligand (I)

Ligand	Chemical Shifts (ppm)			
	OH	CO-NH-	CH=N	C-H Aromatic
I	12.558 (s,2H)	11.642 (s,2H)	9.095 (s,2H)	8.426 - 7.184 (m,19 H)

3.2 Results and Discussion :

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 complexation reaction of necessity behave among many optimum condition to reach equilibria and giving stable ionpair complex .

3.2.1 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 (1×10^{-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 the organic 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 $\text{pH}_{\text{extraction}}$ 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 at pH values more than optimum value effect to decrease distribution ratio (D) and percentage of extraction (E) by reason of formation ion pair complex contain anion (OH^-) this complex more soluble in aqueous phase and less extracted to organic phase and sovereignty the dissociation equilibria

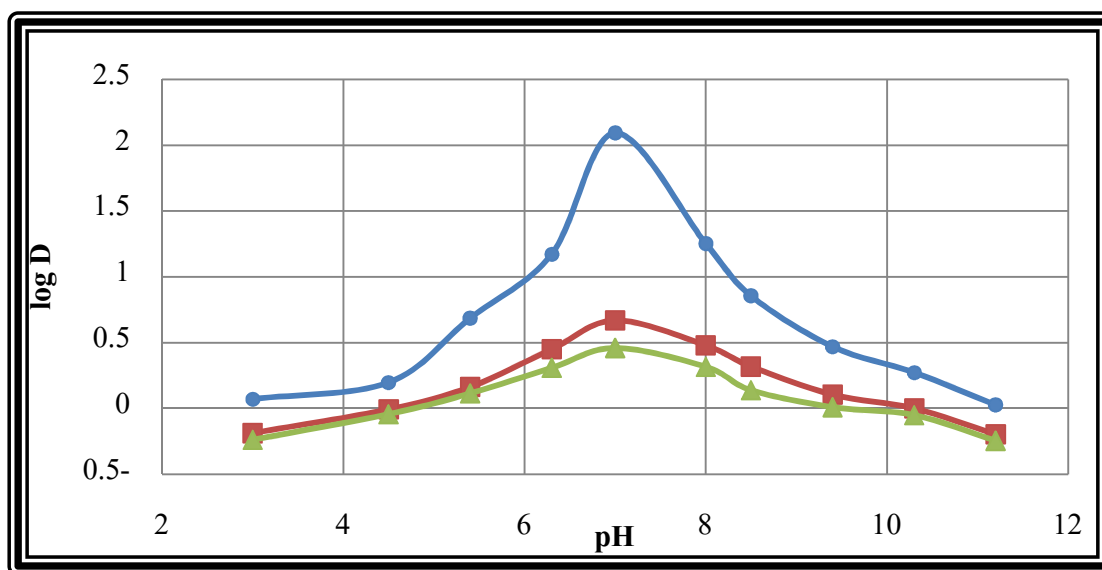


Fig. (5): pH effect on the extraction of Cr(III), Co(II), Cd(II) ions

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

pH	Cd ⁺²			Co ⁺²			Cr ⁺³		
	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

3.2.2. 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 (1×10^{-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.

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	-	0.397	28.41	-0.329	0.468	31.9	-	0.931	48.2
	0.401						0.031		
20	-	0.629	38.6	-0.117	0.764	43.3	0.080	1.203	54.6
	0.201								
30	-	0.718	41.8	0.031	1.075	51.8	0.209	1.62	61.8
	0.144								
40	-	0.988	49.7	0.151	1.416	58.6	0.545	3.505	77.8
	0.005								
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	46.61	97.9
70	0.225	1.68	61.7	0.359	2.289	69.6	1.167	14.67	93.7
80	0.136	1.369	57.8	0.202	1.591	61.4	0.743	5.536	84.7
90	-	0.938	48.39	0.101	1.262	55.8	0.515	3.274	76.6
	0.028								
100	-	0.728	42.12	-0.007	0.984	49.6	0.316	2.068	67.4
	0.138								
110	-	0.610	37.9	-0.131	0.739	42.5	0.159	1.445	59.1
	0.215								
120	-	0.411	29.67	-0.286	0.518	34.1	-	0.905	47.5
	0.386						0.043		

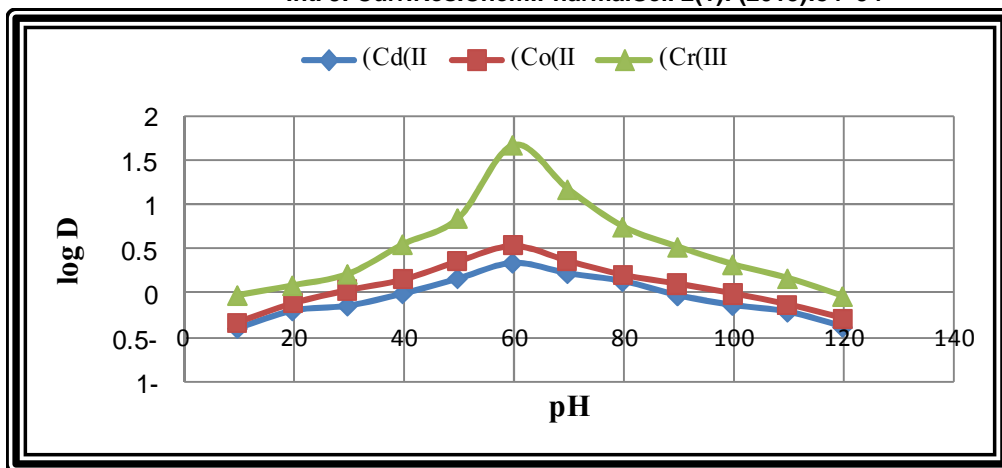


Fig. (6): Effect of shaking time on the extraction of Cr(III), Co(II), Cd(II) ions

3.2.3. Stoichiometry by Slope Analysis Method:

To knowing the more probable structure of Cr(III), Co(II), Cd(II) ion pair complex produced, extracted (1×10^{-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 (2×10^{-5} M – 3×10^{-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).

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	

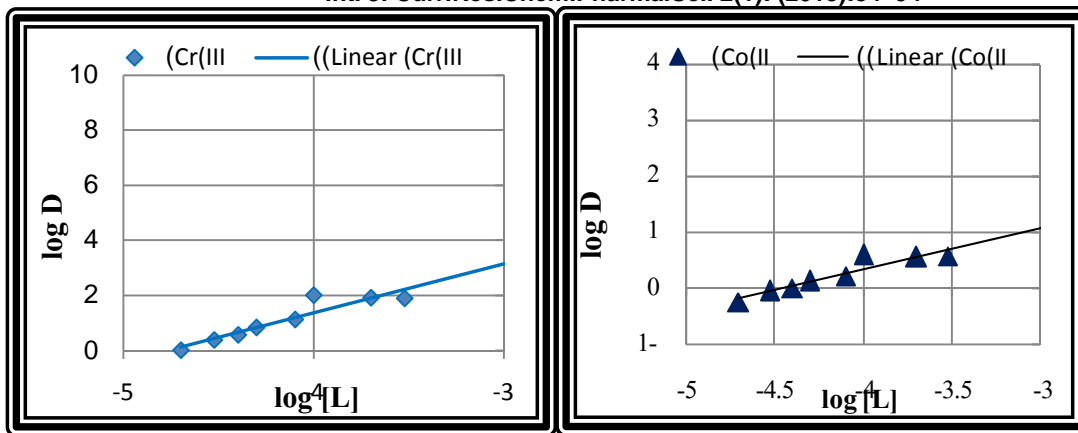


Fig. (7): Slope analysis method for extraction of Cr(III),Co(II) ions

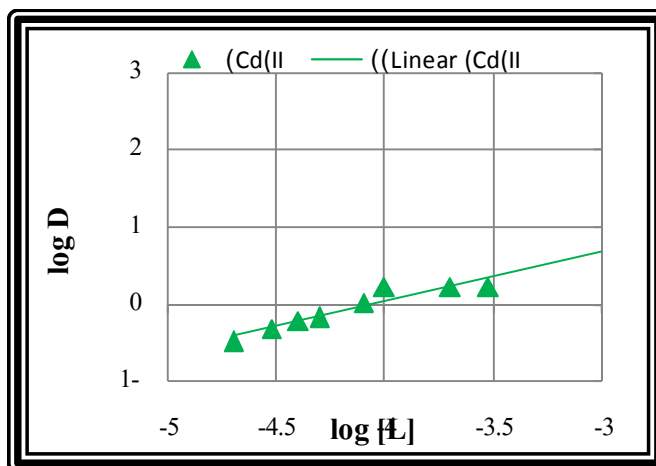


Fig. (8): Slope analysis method for extraction of Cd(II) ions

3.2.4. 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).

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

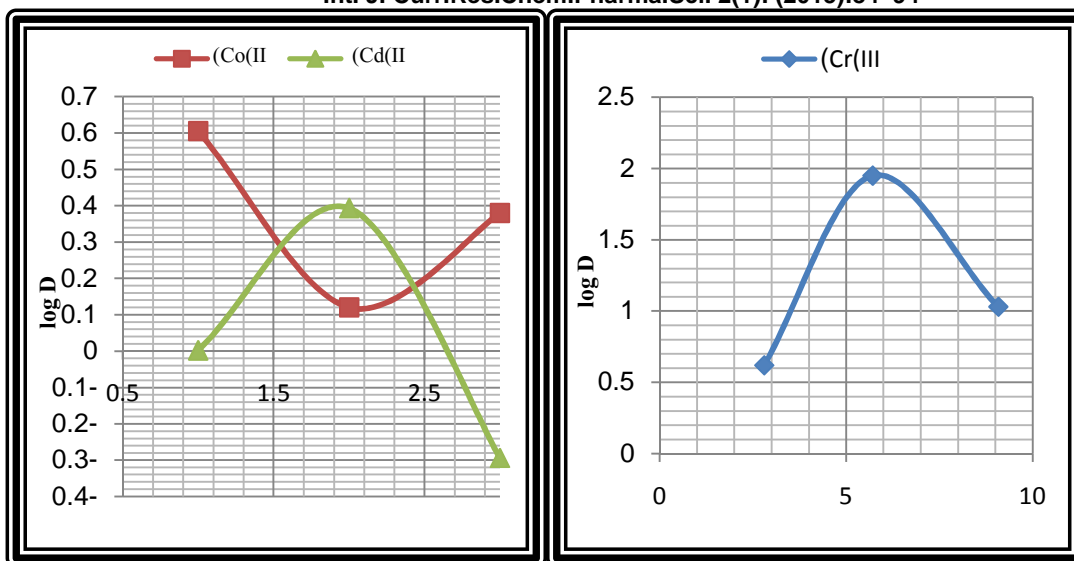


Fig. (8): Effect of solvents organic on the extraction of Cr(III), Co(II), Cd(II) ions

3.6 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 (1×10^{-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.

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

T.C ₀	T.K ⁰	1/T x 10 ⁻³ K ⁰	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

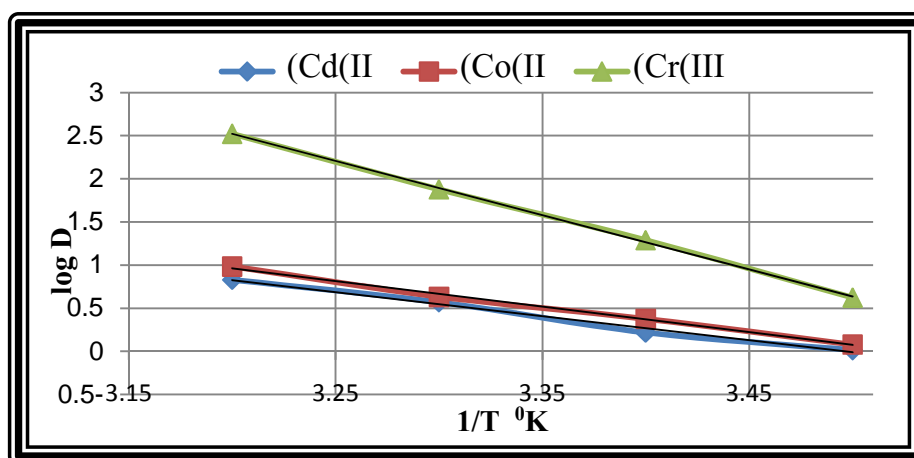


Fig. (9): Temperature effect on the extraction of Cr(III), Co(II), Cd(II) ions

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

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

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

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

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

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

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

Cation	K_{ext}	S_{ext} $\text{JK}^{-1}\text{mol}^{-1}$	G_{ext} kJmol^{-1}	H_{ext} kJmol^{-1}
Cr(III)	276.1×10^{12}	608.63	-86.53	103.97
CO(II)	10.26×10^7	337.86	-47.99	57.76
Cd(II)	52.9×10^6	314.44	-46.28	52.14

Conclusion

- 1- The compound is new and were prepared for the first time.
- 2- The new compound was identified by $^1\text{H-NMR}$, IR, LC-MS, GC-MS, Elemental analysis, and UV-Vis spectral methods.
- 3-The compound showed a high draw ratio of Cr(III), Co(II), Cd(II) ions at $\text{pH} = 7$ 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 over time is better for men, 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 may lead 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 ions correlation between Cr(III), Co(II), Cd(II) and composite studied by Molar (cation: ligand (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, constant

extraction(K_{ex}), 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 all cations studied endothermic (Endothermic), as indicated negative values of energy free to spontaneous reactions, as also indicated positive values of entropy system that many random.

References

1. Zollinger, H. (1991). Color Chemistry, VCH, Weinheim.
2. Hamon, F., Djedaini-Pilard, F., Barbot, F. &Len,C. (2009). Azobenzenes-synthesis and carbo-hydrate application. Tetrahedron, 65, 10105-10123.
3. Gordon, P. F. (1990). The Chemistry and Application of Dyes (Topics in Applied Chemistry)(Warning, D. R.; Hallas, G. Eds.), New York, Plenum Press, P. 381.
4. Patai, S. (Ed.). (1997). The Chemistry of the Hydrazo, Azo and Azoxy Groups, Vol. 2, John Wiley & Sons, Chichester.
5. Carey, F. A. (2000). Organic Chemistry, 4th Ed, New York, McGraw-Hill, P. 896.

6. Pathak, P., Jolly, V. S. & Sharma, K. P. (2000). Synthesis and biological activities of some new substituted arylazo Schiff bases. *Orient. J. Chem.*, 16, 161-162.
7. Xu, H. & Zeng, X. (2010). Synthesis of diarylazo derivatives as potential antifungal agents. *Bioorg. Med. Chem. Lett.*, 20, 4193-4195.
8. Samadhiya, S. & Halve, A. (2001). Synthetic utility of Schiff bases as potential herbicidal agents. *Orient. J. Chem.*, 17, 119-122.
9. Tonelli, M., Vazzana, I., Tasso, B., Boido, V., Sparatore, F., Fermeglia, M., Paneni, M. S., Posocco, P., Pricl, S., Colla, P., Ibba, C., Secci, B., Collu, G. & Loddo, R. (2009). Antiviral and cytotoxic activities of aminoarylazo compounds and aryltriazene derivatives. *Bioorg. Med. Chem.*, 17, 4425-4440.
10. Rani, P., Srivastava, V. K. & Kumar, A. (2004). Synthesis and antiinflammatory activity of heterocyclic indole derivatives. *Eur. J. Med. Chem.*, 39, 449-452.
11. Iranpoor, N., Firouzabadi, H., Khalili, D. & Motevalli, S. (2008). Easily prepared azopyridines as potent and recyclable reagents for facile esterification reaction: an efficient modified Mitsunobu reaction. *J. Org. Chem.*, 73, 4882-4887.
12. Antonov, L. M., Kurteva, V. B., Simeonov, S. P., Deneva, V. V., Crochet, A. & Fromm, K. M. (2010). Tautocrowns: a concept for a sensing molecule with an active side-arm. *Tetrahedron*, 66, 4292-4297.
13. Yildiz, E. & Boztepe, H. (2002). Synthesis of Novel Acidic Mono Azo Dyes and an Investigation of Their Use in the Textile Industry. *Turk. J. Chem.*, 26, 897-903.
14. Stray, J., 1964. *The Solvent Extraction of Metal Chelates*, first ed. The MacMillan Company, p. 1. US Environmental Protection Agency (EPA), 2004. *Separation Techniques*. USEPA.
15. Yaftian, M.R., Taheri, R., Zamani, A.A., Matt, D., 2004. Thermodynamics of the solvent extraction of thorium and europium nitrates by neutral phosphorylated ligands. *J. Radioanal. Nucl. Chem.* 262 (2), 455.
16. Lakshmi, A. K. N. Shivananda, K.N, Gouda Avaji Prakash, Arun M Isloor, and K. N. Mahendra (2012). Synthesis and Characterization of Schiff Base Metal Complexes and Reactivity Studies with Maleimide Epoxy Resin, *Bull. Korean Chem. Soc.* Vol. 33, No. 2.
17. Khanmohammadi H, Darvishpour M., 2009., New azo ligands containing azomethine groups in the pyridazine-based chain: synthesis and characterization. *Dyes Pigm.*, 81:167e73.
18. Dinçaple H, Toker F, Durucasu I, Avcibas, N, Icli S., 2007., New thiophene-based azo ligands containing azo methine group in the main chain for the determination of copper(II) ion. *Dyes Pigm.*, 75:11e24.
19. Salih, I., Hamid, T., 2008 -The synthesis and spectral studies of macrocyclic Cr(III), Co(II), Cd(II) (II), Ni(II) complexes, *J. Chem*, 6 (2), 227-284.
20. Hamid. H. E (2013), Synthesis and characterization of new azo-schiff bases and study biological activity., *JOURNAL OF CR(III), CO(II), CD(II)* Recent research in science (ISSN 2322-5009) 3102, Vol. 1, No. 2, pp:96-103.
21. Bülent .D., Fatma. K., Mustafa. C., 2009- Novel homo- and hetero-nuclear copper(II) complexes of tetradentate Schiff bases: Synthesis, characterization, solvent-extraction and catalase-like activity studies., *Journal of Hazardous Materials* 163, 1148–1156.
22. E. Arifien, A. H. Amerallah, R. M. Awadullah and S. M. Sirro, <http://www.acadjournal.com/2003/part2/p2> internate