

Synthesis and Antibacterial Evaluation of Some Azo-Schiff Base Ligands and Estimation the Cadmium Metal by Complexation

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ABSTRACT

The present paper describes the synthesis of four azo-Schiff base named (1a-4a) by diazotization reaction of the synthesized Schiff bases with sulfonamide compound. All new synthesized derivatives were identified by melting points, CHNS, FT-IR and ¹H-NMR spectra. All compounds were tested for their antibacterial activity that showed good activity. The synthesized compounds were used as sensitive and selective analytical reagent for the spectrophotometric determination of cadmium (II). The calibration curve is linear between 0.05 and 30 µg.ml⁻¹ and limit of quantification, LOQ of (1.203, 1.078, 1.443 and 0.875) µg.ml⁻¹ with molar absorptivity and Sandal's sensitivity values of ligands 2.4778x10⁴, 1.6740x10⁴, 1.70019x10⁴, 1.9002 x10⁴ L mol⁻¹ cm⁻¹ (0.049x10⁻⁴, 0.169x10⁻⁴, 0.132x10⁻⁴, 0.110 x10⁻⁴ µg.cm⁻², for 1a, 2a, 3a

and 4a, respectively. The composition of the Cd (II) - (1a, 2a, 3a and 4a) complex is established as 1:2 by molar ratio and job methods. An excellent linearity with a correlation coefficient value of (0.9997, 0.9996, 0.9974 and 0.9985) is obtained for the complexes.

Keywords: Azo-Schiff base, Cadmium, diazotization, Absorption spectra, Mole ratio

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INTRODUCTION

Azo-Schiff bases are compounds having both azo and azomethine groups. The azo group possesses excellent donor properties which are important in coordination chemistry [1]. It has good donor properties and can form stable complexes with transition metal ion [2]. Azo – Azomethine compounds are new (age) compares with azo and Schiff base [3] that have the dual functional groups at nitrogen atom with non-bonding electron pair [(-N=C-) and (-N=N-)] that owned it special chemical and physical properties. Azo-Schiff compounds can coordinate in many ways, first of them; it can coordinate via azomethine nitrogen [4], secondly by using the two type of nitrogen atoms (azomethine and azo) [5] and finally by the utilizing of azo nitrogen [6] only.

Significant health risks such as kidney failure, hepatitis and lung appear on people who are exposed directly to heavy elements such as cadmium by air, food and water. In addition to the occurrence of damage to the immune and cardiovascular and reproductive systems [7,8]. Studies have shown that cadmium remains in the kidneys (the half-life of 10-30 years) and that the concentration of cadmium is proportional to its concentration in the urine [9].

Symptoms of cadmium poisoning are summarized by high blood pressure, anemia, soreness of the joints, hair loss, dryness and scaling of the skin, and loss of appetite. It also found a clear effect on the infection of laboratory animals with types of cancer, which can be linked to some types of human cancer [10]. Among the dangerous diseases associated with cadmium is a disease of weakened bones and short stature, which gradually leads to the complete collapse of the entire skeletal system [11].

Several laboratory techniques have been used to estimate cadmium voltmetric technology [12], oxidative-reduction methods [13,14], atomic absorption spectroscopy and atomic emission spectroscopy [15-17] and ICP-OES technology has been used [18]. Spectrophotometric

methods are sensitive, easy to handle, low cost, and highly accurate, that distinguish them from routine cadmium estimation techniques.[19]

According to this importance, some of new azo Schiff bases have been synthesized as ligands starting from o-vanillin with primary amines and then formation new azo Schiff bases as a ligand that used for complexation with cadmium metal in solution at low concentration. This method used to determine the metal concentration using spectroscopy methods.

EXPERIMENTAL

Apparatus

For absorbance studies, a Double beam UV-Visible spectrophotometer (Systronics model UV-2203) with a 1.0 cm quartz cell is used. Melting point apparatus used to determine the melting point of Schiff bases and azo-Schiff ligands. Infrared spectra (in KBr pellets) were recorded on a FTIR 8400S SHIMADZU (Japan) in College of Pharmacy, Basrah University. ¹H NMR spectrum of the ligands is recorded on Inova 500 MHz NMR spectrometer (Tehran University-Iran) by using TMS as an internal standard and DMSO-6d as a solvent. The elemental microanalysis was carried out on Eager 300 for EA1112 CHN analyzer at Tehran University, Iran. All glassware are washed with a mixture of concentrated sulfuric acid and nitric acid (1:1) before used.

Reagents and solutions

All chemical used were analytical agents supplied from Sigma-Aldrich. Solvents used were distilled and purified before used. The Schiff base and azo Schiff bases are synthesized by using equimolar grade and of highest purity available and used without purification. Azo Schiff base is complexes with cadmium metal. The metal complexes are stable at normal conditions.

General Procedure for Synthesis of Schiff Bases

4-((2-hydroxy-3-methoxybenzylidene)amino)benzoic acid (1), 4-((2-hydroxy-3-methoxybenzylidene)amino)benzenesulfonamide (2) N-(4,6-dimethylpyrimidin-2-yl)-4-((2-hydroxy-3-methoxybenzylidene)amino)benzenesulfonamide (3) and 4-((2-hydroxy-3-methoxybenzylidene)amino)-N-(5-methylisoxazol-3-yl)benzenesulfonamide (4) were synthesized by same procedure [20].

Schiff bases (1-4) were prepared by the reaction of four primary amines (p-aminobenzoic acid, sulfanilamide, sulfamethazine and sulfamethoxazole) (0.02 mol) with o-vanillin (0.02 mol) in 50 ml ethanol and few drops of glacial acetic acid. This mixture was refluxed for 3 hrs, the solid mass formed was filtered and purified by recrystallization from ethanol, as shown in Figure 1. The physical properties of the products are showed in Table 1.

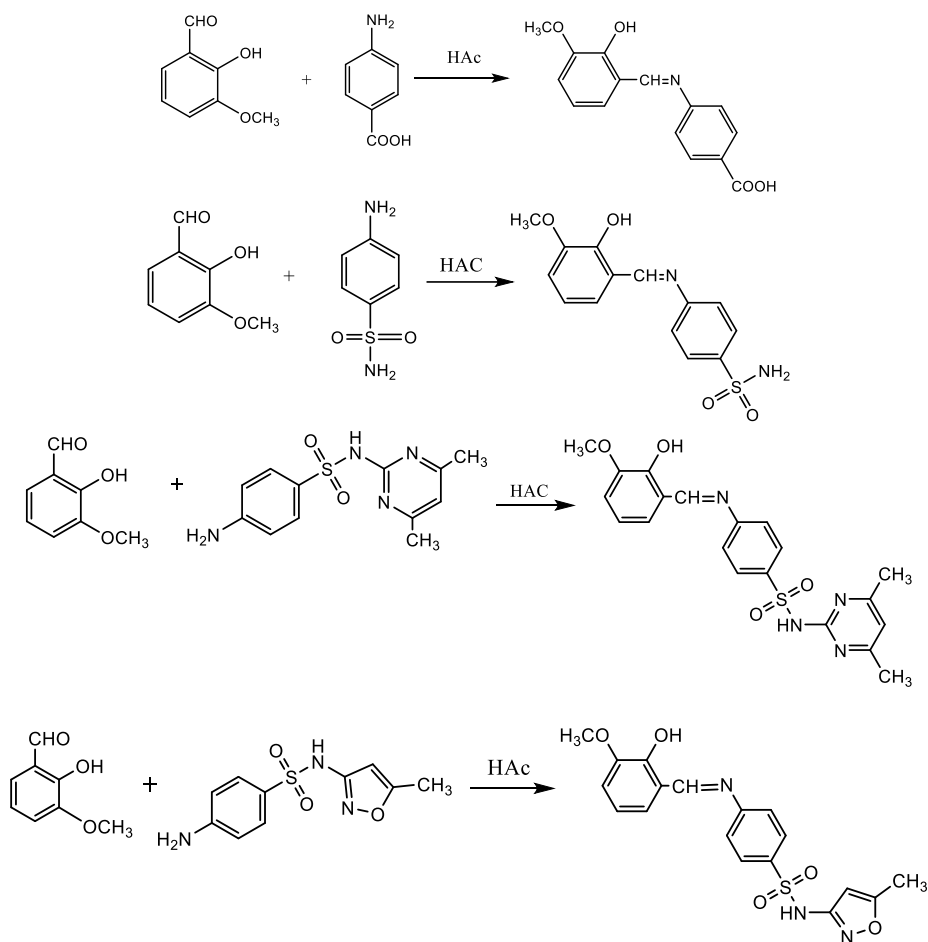


Figure 1: Synthesis of Schiff bases compounds 1-4

Synthesis of Azo Compounds

4-((2-hydroxy-3-methoxy-5-((E)-(4-sulfamoylphenyl) diazenyl) benzylidene) amino) benzoic acid (a1), 4-((1E)-(4-hydroxy-3-methoxy-5-(((4-sulfamoylphenyl)imino) methyl)phenyl) diazenyl) benzenesulfonamide (2a), 4-((E)-(3-((E)-((4-(4,6-dimethylpyrimidin-2-yl)sulfonyl)phenyl) imino) methyl)-4-hydroxy-5-methoxyphenyl) diazenyl) benzenesulfonamide (3a) and 4-((1E)-(4-hydroxy-3-methoxy-5-(((4-((5-methylisoxazol-3-yl) sulfonyl) phenyl) imino) methyl) phenyl) diazenyl) benzenesulfonamide (4a) were prepared by same procedure [21, 22], as shown in Figure 2.

Sulfanilamide (0.69 g, 0.004 mol) was dissolved in dilute hydrochloric acid, stirred vigorously while being cooled to 0 °C. A solution of sodium nitrite (0.28 g, 0.004 mol) in distilled water was added drop wise to the reaction mixture and the solution was kept below 0 °C. KOH (0.224 g, 0.004 mol) was dissolved in ethanol and was added Schiff base (0.004 mol) with constant stirring. This solution was added drop wise to diazotized sulfanilamide. The solution was cooled to 0 °C. The solid product was collected and recrystallized from ethanol. The characterizations of the products are listed in Table 1.

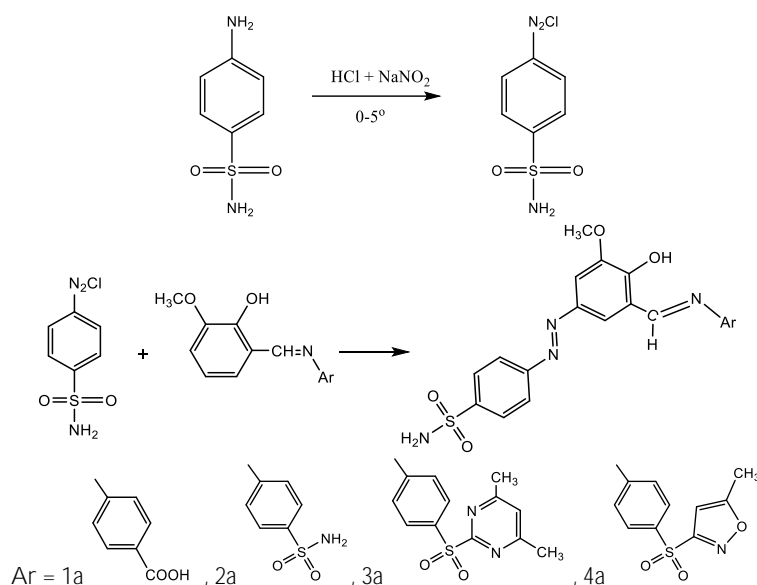


Figure 2: Synthesis of Azo-Schiff bases compounds 1a-4a

Table 1: Physical properties of the synthesized compounds

Compd.	Molecular formula	Molecular weight (g/mole)	Crystal color and shape	m.p. (°C)	Yield (%)
1	C ₁₅ H ₁₃ NO ₄	271.27	yellow crystal	195	90
1a	C ₂₁ H ₁₈ N ₄ O ₆ S	454.46	Orange crystal	<300	85
2	C ₁₄ H ₁₄ N ₂ O ₄ S	306.34	pale yellow crystal	205	70
2a	C ₂₀ H ₁₉ N ₅ O ₆ S ₂	489.52	Red crystal	<300	68
3	C ₂₀ H ₂₀ N ₄ O ₄ S	412.46	yellow crystal	210	80
3a	C ₂₆ H ₂₅ N ₇ O ₆ S ₂	595.65	Dark brown	<300	77
4	C ₁₈ H ₁₇ N ₃ O ₅ S	387.41	yellow crystal	188	85
4a	C ₂₄ H ₂₂ N ₆ O ₇ S ₂	570.60	Red crystal	<300	72

Preparation of metal solution and reagent solution

A 100-mL amount of stock solution (1 mg mL⁻¹) of divalent cadmium was prepared by dissolving 0.2282mg of pure crystallized cadmium sulfate in doubly distilled de-ionized water., add 3 ml of 1.5 × 10⁻⁵ M ethanolic (azo-Schiff compounds) solution and diluted to the mark with water. Measure the absorbance of the resultant solution after 3 min. at 410, 440, 460 and 470 nm at 25°C against blank solution prepared by the same procedure.

RESULTS AND DISCUSSION

Elemental analysis (CHNs) of the azo-Schiff compounds are summarized in Table 2. The results showed that the analysis findings are closely related to the calculated values, ensuring that the correct methods of the compounds and the high purity of the compounds.

Table 2: Elemental analysis of the synthesized azo-Schiff compounds

Compd.	Molecular formula	Molecular weight (g/mole)	Calculated				Found			
			C%	H%	N%	S%	C%	H%	N%	S%
1	C ₁₅ H ₁₃ NO ₄	271.27	54.89	4.61	9.14		55.24	4.52	8.94	
1a	C ₂₁ H ₁₈ N ₄ O ₆ S	454.46	55.50	3.99	12.33	7.05	54.86	4.05	12.57	7.11
2	C ₁₄ H ₁₄ N ₂ O ₄ S	306.34	54.89	4.61	9.14	10.46	54.68	4.52	9.31	10.23
2a	C ₂₀ H ₁₉ N ₅ O ₆ S ₂	489.52	49.07	3.91	14.31	13.09	49.41	3.84	14.25	12.99
3	C ₂₀ H ₂₀ N ₄ O ₄ S	412.46	58.24	4.89	13.58	7.77	58.12	4.75	13.64	7.81
3a	C ₂₆ H ₂₅ N ₇ O ₆ S ₂	595.65	52.43	4.23	16.46	10.76	52.12	4.35	16.54	10.83
4	C ₁₈ H ₁₇ N ₃ O ₅ S	387.41	55.81	4.42	10.85	8.27	56.01	4.47	10.90	8.36
4a	C ₂₄ H ₂₂ N ₆ O ₇ S ₂	570.60	50.52	3.89	14.73	11.23	50.42	3.94	14.62	11.34

FT-IR Spectra

I.R spectra can enhanced in interoperation of the functional groups in organic compounds, due to highly interference in the bands of the functional groups that azo owned compounds in (1700-1400 cm^{-1}) region we depend on many references [20-22] in the identification, to determine the stretching bands of the ligand groups.

IR spectra of all compounds exhibited prominent peaks at 3267-3302 cm^{-1} , 1613-1634 cm^{-1} , 1445-1454 cm^{-1} ascribed to $\nu_{(\text{O-H})}$, $\nu_{(\text{CH=N})}$ and $\nu_{(\text{N=N})}$ vibrations, respectively. In addition, the stretching vibration due to $\nu_{(\text{C-O})}$ band overlapping with $\nu_{(\text{C-N})}$ band appeared at 1157-1284 cm^{-1} in the azo-Schiff base ligand [23], as shown in Table 3.

Table 3: Characterized bands in FT-IR spectra for prepared compounds

1a	2a	3a	4a	Assignment
3295 b	3302 b	3287 b	3267 b	O-H stretching
3056 w	3091 w	3067 w	3102 w	C-H stretching aromatic
1626 s	1634 s	1613 m	1618 m	C=N stretching of ring
1548 w 1460 m	1551 m 1478 m	1550 m 1482 s	1487 m	C=C stretching of aromatic rings
1445 m	1448 m	1454 w	1450 m	N=N stretching ring
1271 m 1165 m	1284 m 1163 m	1256 m 1157 m	1253 m 1161 m	C-O and C-N stretching
633 m	628 m	613 m	611 m	C-H bending aromatic

br = broad, s = strong, m = medium, w = weak

$^1\text{H-NMR}$ Spectra of Ligands

The data of $^1\text{H-NMR}$ Spectra of prepared compounds are shown in Table 4. The $^1\text{H-NMR}$ spectra of (1a, 2a, 3a and 4a) compounds used performed in DMSO-d_6 were showed in Figures 3-6. These spectra showed upland signals at 2.5 and 3.3 ppm related to protons solvent and water in solvent. The $^1\text{H-NMR}$ spectra of all compounds gave a singlet signal at the range 10.070-10.397 ppm assigned to the proton of phenolic -OH group. The multiple signals 6.953-8.135 ppm

are due to the aromatic protons. Also the singlet signals at 8.871, 8.618, 8.461 and 8.494 ppm are assigned to the proton of (HC=N) group of the compound (1a, 2a, 3a and 4a), respectively. The singlet signals at two ranges 6.029-6.530 ppm and 3.834-4.000 ppm referred to the protons of sulfonamide and methoxy groups, respectively. The compound 1a has download signal at 11.227 ppm related to proton of carboxyl group.

Table 4: Data for $^1\text{H.NMR}$ spectra δ (ppm) of azo-Schiff compounds

Com pd.	-CH ₃	-OCH ₃	-SO ₂ NH ₂	Arom. H	-CH=N-	-OH	-COOH
1a	-	3.982 (3H, s)	6.029 (2H, s)	7.251-8.059 (10H, m)	8.871 (1H, s)	10.397 (1H, s)	11.227 (1H, s)
2a	-	3.928 (3H, s)	6.530 (4H, s)	7.515-8.135 (10H, m)	8.618 (1H, s)	10.394 (1H, s)	-
3a	3.044 (6H, s)	4.000 (3H, s)	6.284 (2H, s)	7.090-7.929 (11H, m)	8.461 (1H, s)	10.070 (1H, s)	-
4a	3.129 (3H, s)	3.834 (3H, s)	6.113 (2H, s)	6.953-7.929 (11H, m)	8.494 (1H, s)	10.183 (1H, s)	-

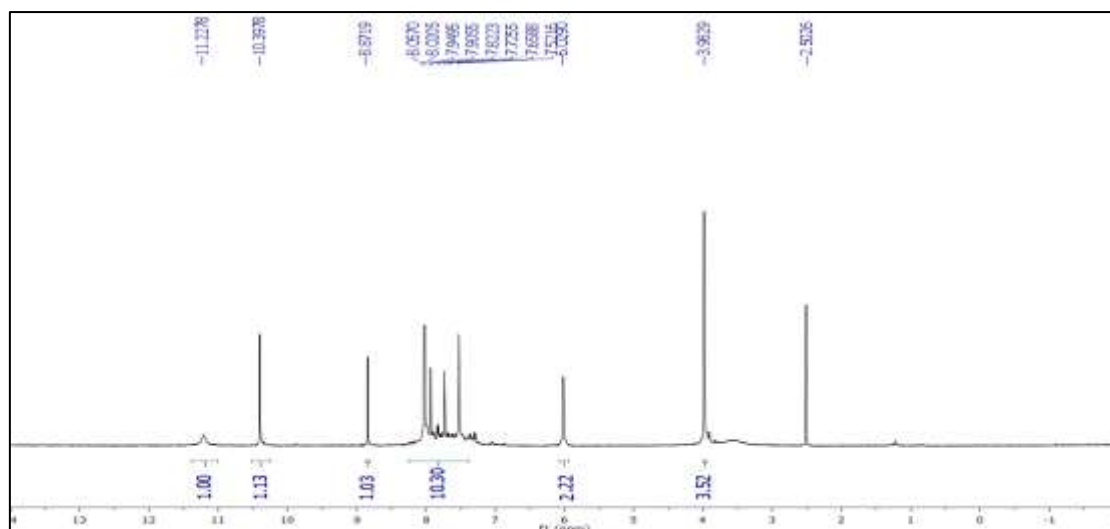


Figure 3: 1H-NMR spectrum of 1a compound

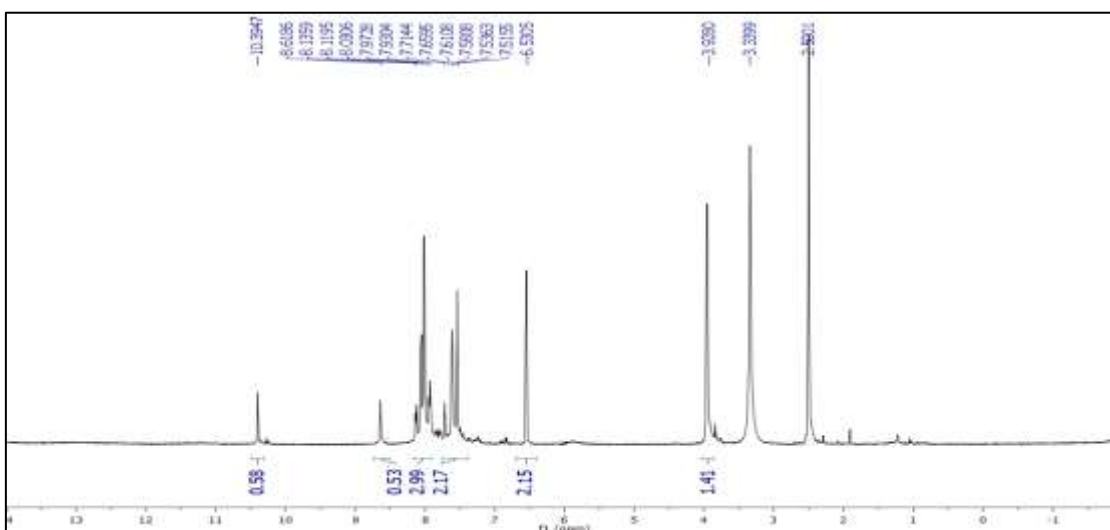


Figure 4: 1H-NMR spectrum of 2a compound

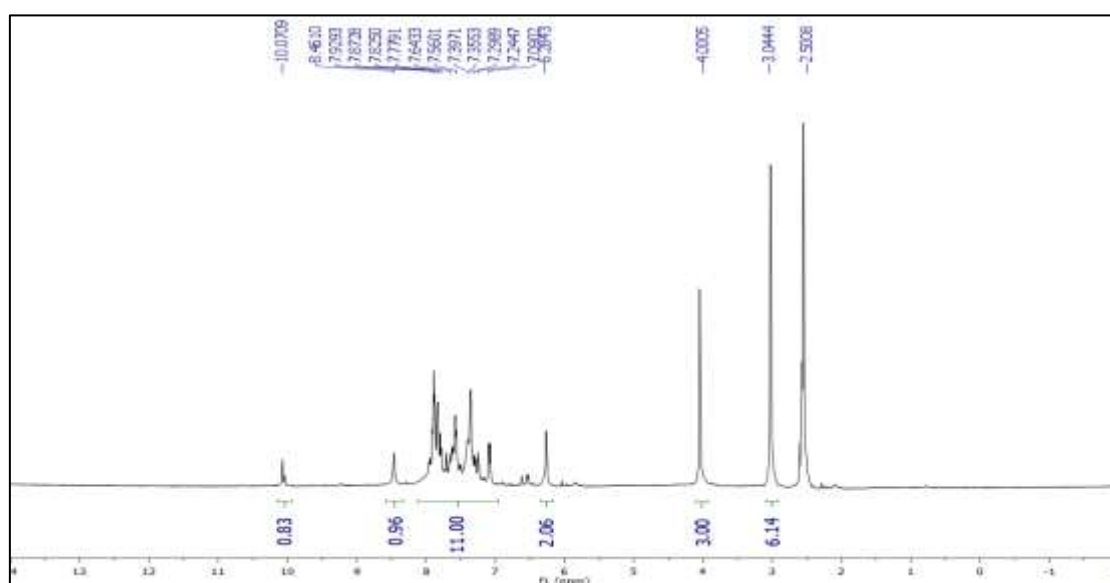


Figure 5: 1H-NMR spectrum of 3a compound

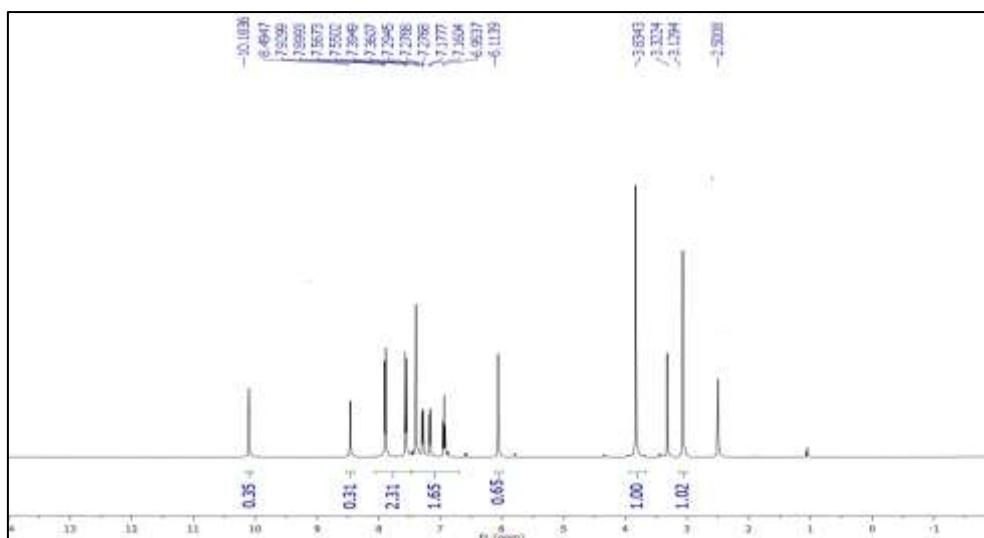


Figure 6: 1H-NMR spectrum of 4a compound

Antibacterial activity

All synthesized compounds (1-4 and 1a-4a) were tested their antibacterial activity in University of Basrah / College of Science / Department of Biology using two *G+ve* bacteria (*Staphylococcus aureus*, *Streptococcus* spp.) and two *G-ve* bacteria (*Escherichia coli* and *Klebsiella pneumonia*) by the diffusion technique. Filter paper disc of (6 mm) which impregnated with specified concentrations (500 µg / mL, 750µg / mL and 1000µg/mL) in DMSO solvent. The results

of measuring the diameter of the inhibition area after 24 hours at 37°C was represents in Table 5.

It was noticed from the results that the zone of inhibition increased with increase in concentration, so for high concentration (1000 µg/ml). The azo-Schiff compounds had potent activity than the corresponding Schiff base compounds. At (1000 µg/ml), compound 4a had inhibition zone 14-18 mm against all bacterial strains, while compound 1 had the lower activity.

Table 5: Inhibition zone of Azo-Schiff base derivatives (1a-4a) against tested bacteria

Compd.	Conc. (µg/ml)	<i>S.aureus</i>	<i>Str. spp</i>	<i>K.pneumonia</i>	<i>E.coli</i>
1	1000	11	9	-	-
	750	-	-	-	-
	500	-	-	-	-
2	1000	8	15	14	15
	750	-	12	10	12
	500	-	10	-	-
3	1000	10	11	16	15
	750	-	-	14	12
	500	-	-	12	8
4	1000	12	12	15	16
	750	8	9	14	14
	500	-	-	9	11
1a	1000	12	10	-	11
	750	9	-	-	8
	500	-	-	-	-
2a	1000	13	16	14	14
	750	8	14	11	12
	500	-	10	-	9
3a	1000	12	12	18	15
	750	-	-	16	11
	500	-	-	12	-
4a	1000	16	14	18	18
	750	9	11	16	16
	500	-	9	12	12

Spectroscopic study

The colored solutions of the ligands had absorption spectrum which showed an absorption λ_{max} at 410, 440, 460 and 470 nm for 1a, 2a, 3a and 4a, respectively. (Figure 7).

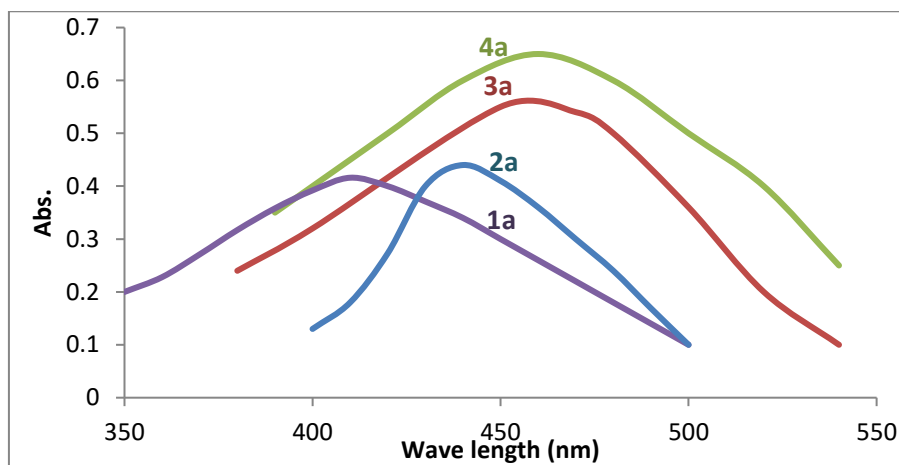


Figure 7: Absorption spectra of 1a 20 $\mu\text{g/ml}$, 2a 20 $\mu\text{g/ml}$, 3a 40 $\mu\text{g/ml}$ and 4a 30 $\mu\text{g/ml}$ under optimum conditions

Analytical validation

Standard solutions of ligands under optimum condition was used to plot the calibration curve. The calibration curves gave a linear relationship between the absorbance and

concentration of dyes in the concentration range 2-25, 1.5-25, 0.05-30 and 0.2-20 $\mu\text{g/ml}$ for the compounds 1a, 2a, 3a and 4a, respectively, as shown in Figure 8.

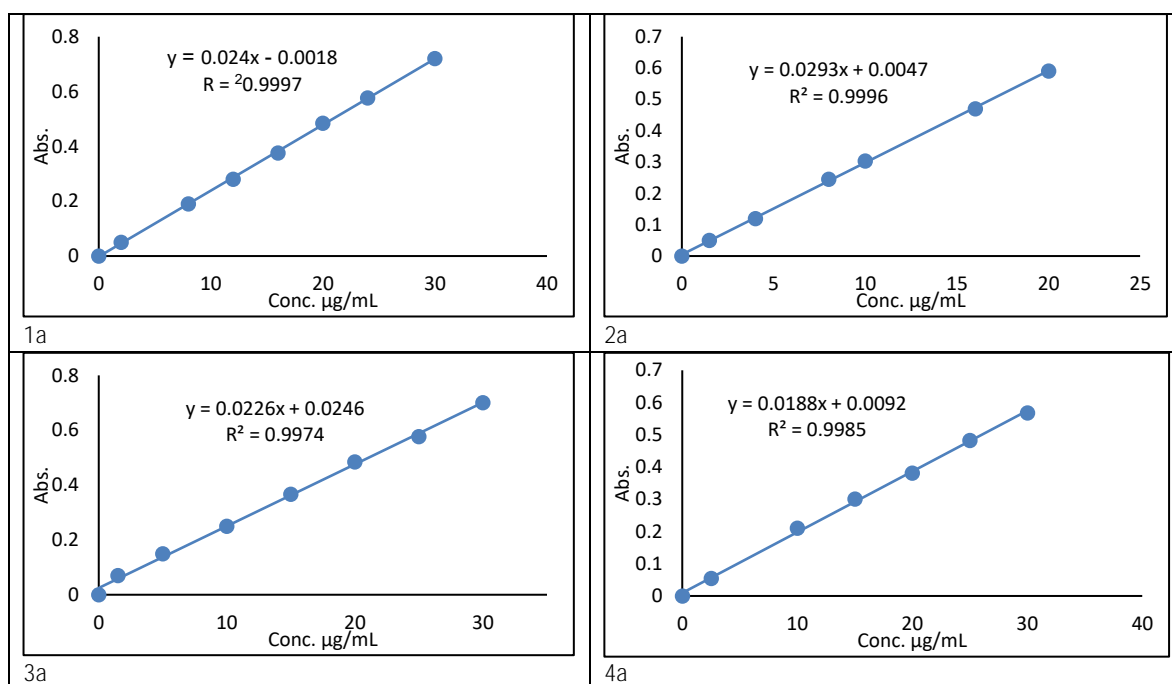


Figure 8: Calibration curves for the determination 1a, 2a, 3a and 4a

The molar absorptivity and Sandal's sensitivity for each dye were calculated from Beer's law. The results of statistical analysis and analytical parameters were referred in Table 6.

The calibration curves had very good correlation coefficient (R) which approximately unity, and represented by the values 0.9997, 0.9996, 0.9974 and 0.9985.

Table 6: Optical characteristics for the determination of 1a, 2a, 3a and 4a compounds

Parameters	Value			
	1a	2a	3a	4a
Measurement wavelength (nm)	410	440	470	460
Linear range ($\mu\text{g ml}^{-1}$)	2.0-25	1.5-25	0.05 -30	0.2-20
Intercept	0.0018	0.0047	0.0246	0.0092
Slope	0.024	0.029	0.022	0.0188
Standard deviation	0.0042	0.0011	0.0001	0.0021
Correlation coefficient (R^2)	0.996	0.996	0.9997	0.996
Molar absorptivity, ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	2.4778×10^4	1.6740×10^4	1.70019×10^4	1.9002×10^4
Sandal sensitivity	0.049×10^{-4}	0.169×10^{-4}	0.132×10^{-4}	0.110×10^{-4}
Limit of quantification ,LOQ ($\mu\text{g.m}^{-1}$)	1.203	1.078	1.443	0.875

The suggested complexes structure

The complexes between the ligand and Cd(II) in solution were investigated by mole ratio and job method [16] at constant maximum absorbance using the optimum conditions of experiment. From these methods, the results showed that the mole ratio is (1:2) of metal:ligands for all

complexes. The analytical results for four complexes were showed in Figures 9-11. Furthermore, there is increasing in the absorbance of the prepared complexes which gave intersection point and after this point the absorbance still constant which indicate clear evidence that the complex was formed and be stable at the certain conditions[17].

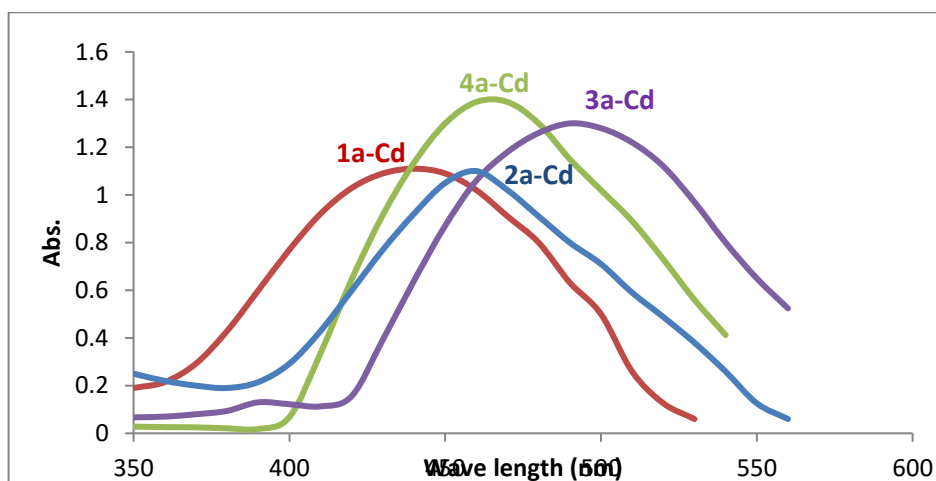


Figure 9: Absorption spectra of 25 $\mu\text{g/ml}$ cadmium-Azo-Schiff complexes in absolute ethanol

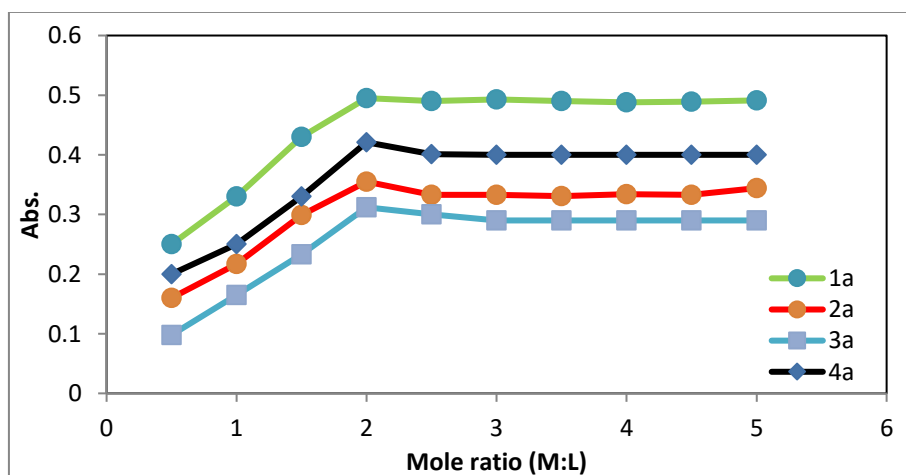


Figure 10: Mole ratio for complexes solutions at optimum conditions

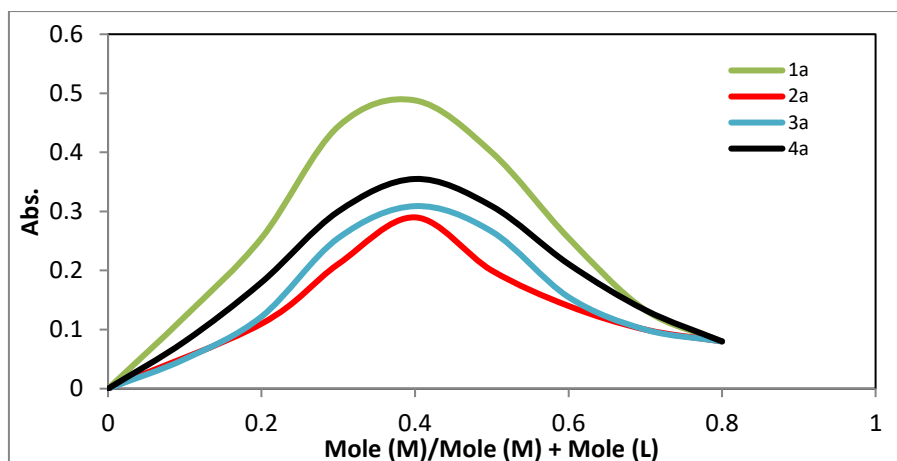


Figure 11: jobs methods for complexes solutions at optimum conditions

The formation of the complexes (ligands:Cd) may be tetrahedral shape, and may be represented by Figure 12.

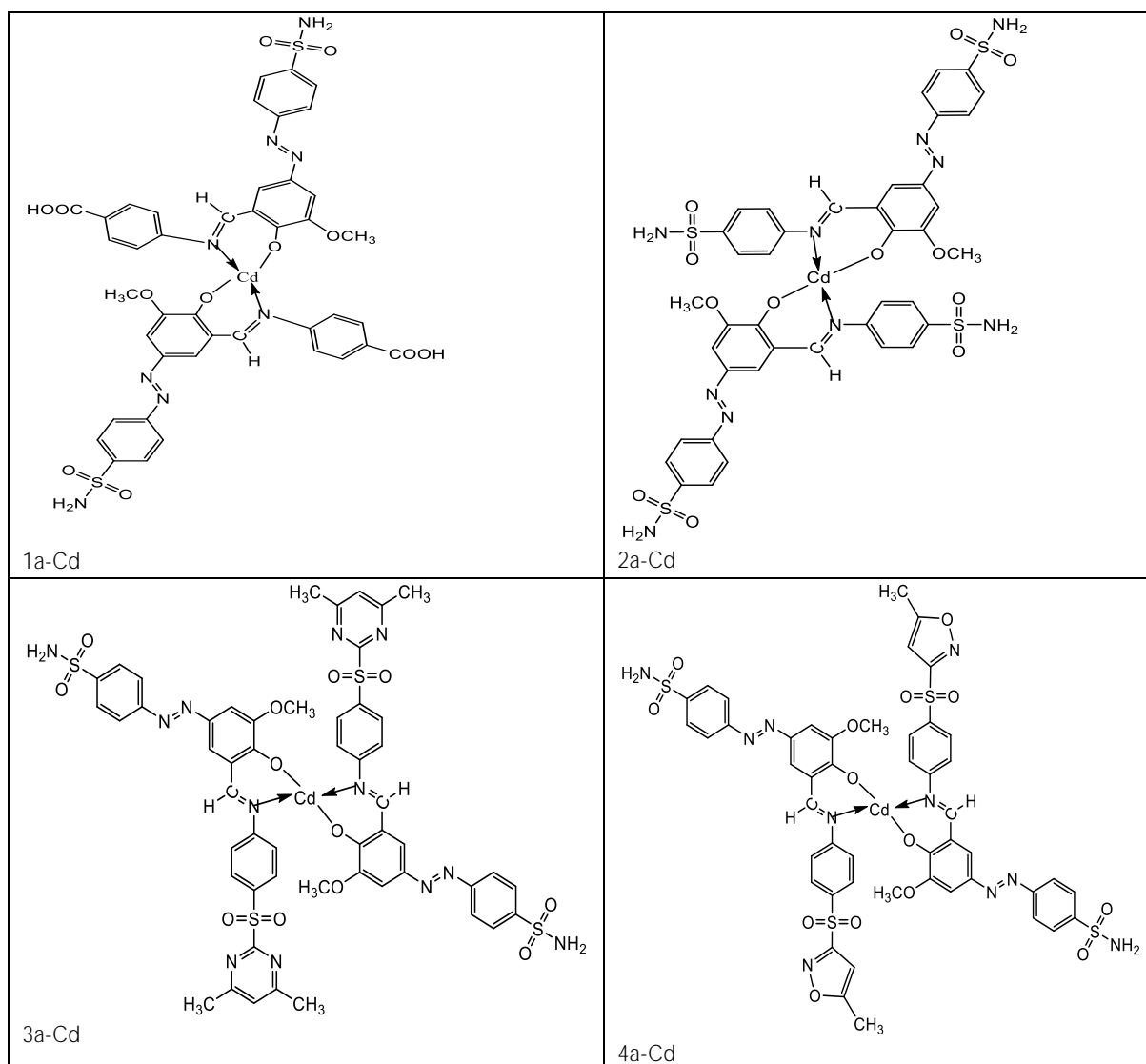


Figure 12: Probably formation structure of complexes

Time effect on the complex formation
The stability of complexes were studied using the max wavelength and under the optimum conditions in the

period time 60 min. The results indicated that these four complexes had good stability in the range (30-50) minutes with stable absorbance value, as showed in Figure 13. It is

evident from Figure 13 that the complexes had stable color change achieved after 30 min.

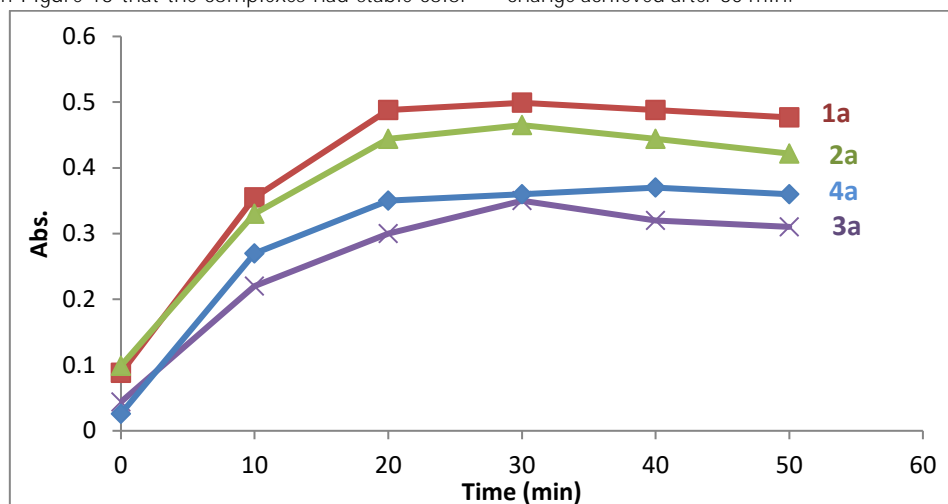


Figure 13: Effect of reaction time on the determination of complexes

CONCLUSION

The (1a, 2a, 3a and 4a) ligand compounds are new and were prepared for the first time. The new compounds were identified by ¹H-NMR, IR and UV-Vis spectral methods. Used ligand compounds a spectrophotometric reagent to determine cadmium is selective, rapid and simple, sensitive and economical. Complex compounds are stable and the method involves less progressing instrumentation.

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