مجلة جامعة تشرين للبحوث والدراسات العلمية – سلسلة العلوم الأساسية المجلد (34) العدد (1) 2012
Tishreen University Journal for Research and Scientific Studies - Basic Sciences Series Vol. (34) No. (1) 2012

Synthesis, Characterization of Imines Derived From Salicyaldehyde and Use Them in Extraction of Some Metal Cations

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(Received 23 / 10 / 2011. Accepted 31 / 1 /2012)

☐ ABSTRACT ☐

Several Schiff bases derived from salicyaldehyde have been synthesized and characterized. The Schiff bases derivatives of saliylidene has been studied by means of elemental analysis, Ms, IR, ^1H and ^{13}C NMR spectra. The spectra are discussed and compared with of compounds N.N-1.2-cyclohexylene bis(salicylideneimine), N.N'-1.2-cyclohexylene bis(5-bromo salicylideneimine) and ,4.4'- diaminodiphenylsulfon bis(salicylideneimine). Strong intramolecular forces are present as supported by the IR and ^1H NMR spectra. Separation of Cu^{2+} and Cr^{3+} from aqueous solution using 4.4'-diaminodiphenylsulfon bis(salicylideneamine) as new solvent for extraction has been studied. The Schiff base has been studied by liquid–liquid extraction towards the metal ions (UO_2^{2+})and d-metal ions (Hg^{2+}, Co^{2+} and Cr^3+) from aqueous phase to organic phase.

Keywords: Synthesis of Schiff bases, Extraction Liquid- liquid, cyclohexyl.

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Tishreen University Journal for Research and Scientific Studies - Basic Sciences Series Vol. (34) No. (1) 2012

اصطناع مشتقات ايمينية من الساليسيل الدهيد واستخدامها في استخلاص بعض الكاتيونات المعدنية

الدكتور عدنان ديب[*]

(تاريخ الإيداع 23 / 10 / 2011. قُبِل للنشر في 31 / 1 /2012)

□ ملخّص □

جرى اصطناع ودراسة عدة مركبات من أسس شيف مشتقة من ساليسيل ألدهيد وشخصت بالتحليل العنصري ومطيافية ما تحت الأحمر والرنين النووي المغناطيسي الهيدروجيني والكربوني. نوقشت وقورنت المطيافية بين مركبات N'.N-2.1-حلقي هكسيل بيس (ساليسيليدين ثنائي الايمين) وN'.N-2.1- حلقي هكسيل ثنائي (5-برمو ساليسيليدين ثنائي الايمين) و 4'.4- ثنائي امين ثنائي فينيل سلفون ثنائي (ساليسيليدين ثنائي الايمين). أكدت النتائج المسجلة لطيوف IR و NMR للمركبات المدروسة وجود روابط قوية بين الجزئيات. درس فصل شوارد معدني الكروم والنحاس من المحاليل المائية باستخدام مركب 4'.4-ثنائي امينو ثنائي فينيل سلفون بيس (ساليسيليدين ثنائي الامين) بوصفه من المركبات الواعدة للاستعمال مستقلاً في استخلاصها والتخلص منها. درس أساس شيف السابق باستخلاص ايونات المعادن الانتقالية بعمليات سائل-سائل تجاه ايونات UO_2^{2+} والمعادن الانتقالية مثل Hg^{2+}, و Co^{2+} و Cr^{3+} لإخراجها من الطور المائي إلى الطور العضوي.

الكلمات المفتاحية: اصطناع أسس شيف، الاستخلاص سائل-سائل، حلقي الهكسيل

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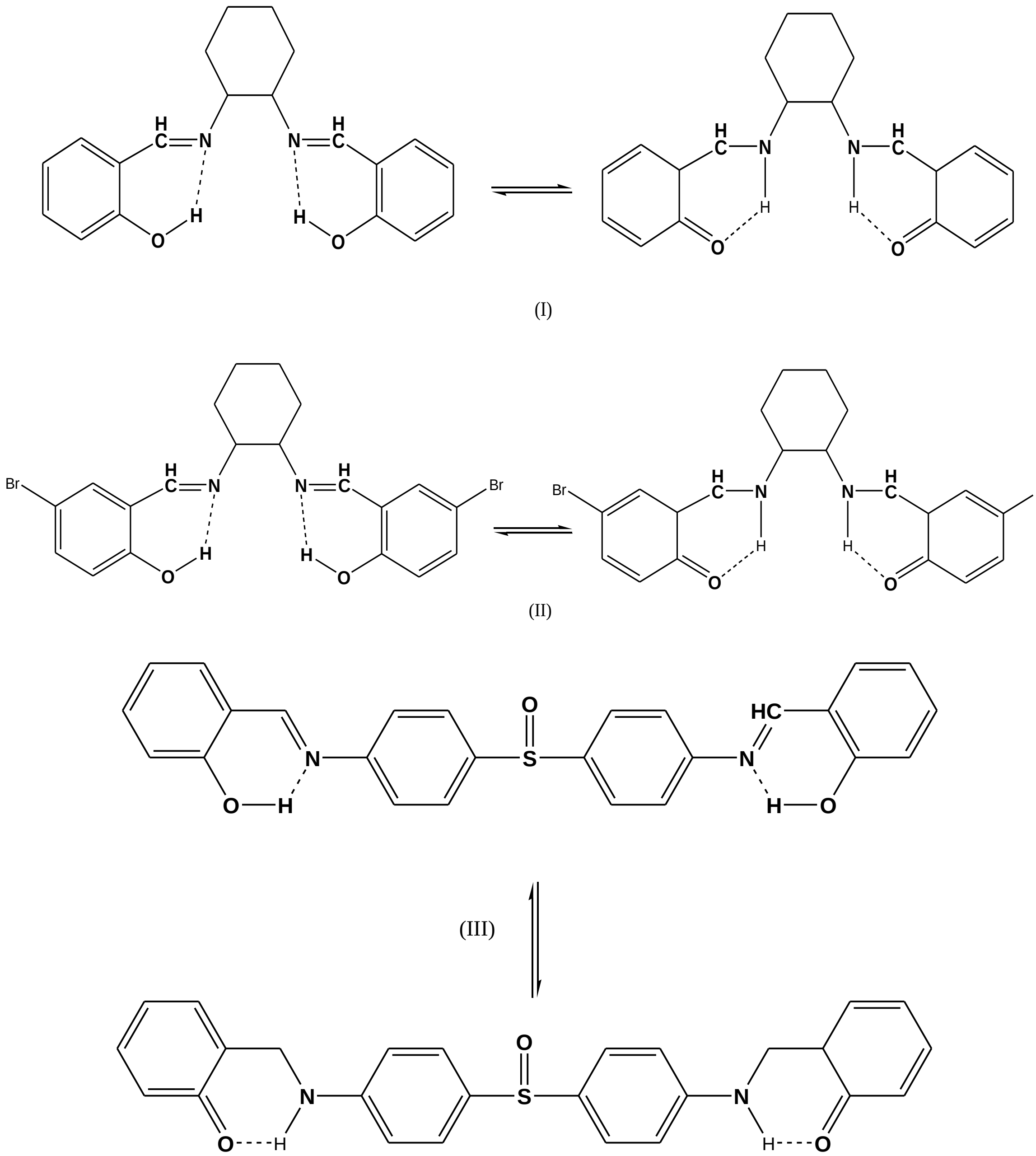
Introduction:

Compounds of Schiff bases have interesting photo-physical properties as thermochromism and photochromism providing potential applications as organic materials for reversible optical data storage. Since these photo-physical properties are governed by intramolecular proton transfer from the hydroxyl O atom to the imine N atom, several studies have focused on the nature of the hydrogen bonding in such compounds [1]. Tautomerism in Schiff bases with OH group in ortho position to the imino group both in solution and in solid state were investigated using spectroscopy and X-ray crystallography techniques [2]. Schiff bases with OH group in ortho position to the imino group are of interest mainly due to the existence of either O-H--N or O--H-N type of hydrogen bond and tautomerism between enolimine and keto-amine form, Fig. 1. The Schiff bases derived from salicylaldehyde generally form the O-H --N type of hydrogen bonding, regardless of the nature of the N-substituent [3]. Compounds derived from 2-hydroxy-1-naphthaldehyde, both types of hydrogen bonds were found [4].

Chelate extraction is a very effective analytical separation method for the metal species in solution [5-11]. Solvent extraction enjoys a favored position among the separation techniques because of its easy, simplicity, rapid and wide scope. Solvent extraction of metal chelate complexes has been used as a separation method for a long time. Copper and chrome are both vital and toxic for many biological systems [12]. Thus, the determination of trace amounts of Cu and Cr are becoming increasingly important because of the increased interest in environmental pollution. Flame and graphite furnace atomic absorption spectrometry and spectrophotometric methods provides accurate and rapid determination of these metals in natural water and waste water. Nevertheless, very frequently for the extremely low concentration these metal ions in water, a direct determination cannot be applied without their previous preconcentration and separation. The most widely used techniques for the separation and preconcentration of trace amounts are liquid-liquid extraction [12], precipitation, sorption [13,14] solid phase techniques [15] and chelating resins [16]. Very often, both separation and preconcentration are required, and an advantage of solvent extraction is that both can be obtained in the same step. Recovery of metals from an aqueous phase with an organic phase that contain a metals selective chelateing agent used has high distribution, coefficient and pH dependence in the system chosen. Reagents such as crown ethers, Schiff bases, oximes, amines and several phosphine oxides can be used as chelating agent [17].

these compounds have short hydrogen bonds between the OH group in ortho position to the imino group and the imine nitrogen are due to the stereochemistry. Whereas strong intramolecular hydrogen bonding is reported to these compounds, short hydrogen bonds between the OH group in ortho position due to the imino group and the imine nitrogen and strong intramolecular hydrogen bonding is reported.

In this present paper, Schiff base derived from salicylidene have reported. The ligands have been synthesized and characterized on the basis of analysis of elemental analyses, IR-spectra, Mass spectra ^{1}H and ^{13}C NMR. Also In this work a newly synthesized 4.4'-diaminodiphenylsulfon bis(salicylideneamine) is studied as an active reagent for extraction Cu^{2+} . Extraction and determination by atomic absorption spectrometry have been reported.



(I)

(II)

(III)

Scheme 1. Synthesis of new Schiff base

Experimentals:

Reagents and Apparatus:

All the chemicals are were of Analar grade, and from Sigma–Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received. Distilled water was used in all experimentals. 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. Mass spectra were recorded using a KRATOS MS50TC spectrometer.

AA 929 Unicam Spectrometer was used for FAAS measurements with an air-acetylene flame. A Shimadzu model UV-160 UV/VIS spectrophotometer with 1.0 cm quartz cell was used for the measurement of absorption spectra. A pH meter (Metrohm 691 pH Meter) was also used. All extractions experiments were performed using a mechanical flask agitator in 50 cm^3 stoppered glass flasks.

Ligand preparation:

2.2.1. Synthesis of N,N'-1,2-cyclohexylene bis(salicylideneamine)(I)

The Schiff base was prepared by condensing salicylaldehyde with the 1,2-diaminocyclohexane using the method described previously[9]. To a stirred solution of 2.44 g (20.0 mmol) of 3-ethoxysalicylaldehyde dissolved in methanol (20 ml) was added dropwise a methanolic solution (10 ml) of (10 mmol) of 1,2-diaminocyclohexane. This mixture was then heated for 2 h. Afterwards the mixture was cooled to room temperature, and then cooled for 24 h at 5 °C. The solid was filtered and washed with cold methanol (5 ml at 5°C) and dried over silica. Yield: 90%; m.p. 139–140°C, Analyses for $C_{20}H_{24}N_2O_2$; C, 74.07; H, 7.40; N, 8.64; Found C, 73.02; H, 7.3; N, 8.62.

2.2.2. Synthesis of N,N'-1,2-cyclohexylene bis(5-bromo salicylideneamine)(II)

The Schiff base was prepared by condensing 5-bromo salicylaldehyde with the 1,2-diaminocyclohexane using the method described previously[9]. To a stirred solution of 5.67 g (20.0 mmol) of salicylaldehyde dissolved in methanol (20 ml) was added dropwise a methanolic solution (10 ml) of (10 mmol) of 1,2-diaminocyclohexane). This mixture was then heated for 2 h. Afterwards the mixture was cooled to room temperature, and then cooled for 24 h at 5 °C. The solid was filtered and washed with cold methanol (5 ml at 5°C) and dried over silica. Yield: 90%; m.p. 139–140°C. Analyses for $C_{20}H_{22}N_2Br_2O_2$; C, 50; H, 4.58; N, 5.83; N, 5.83 Found C, 50.2; H, 4.4; N, 5.7.

2.2.3 synthesis 4,4-diaminodiphenylsulfon bis(salicylideneamine)(III)

The bis-bidentate ligands were prepared by a usual Schiff-base condensation in methanol (50 ml) of salicylaldehyde (10 mmol, 1.22 g) with bridging diamine (4,4-diaminodiphenylsulfon, 5 mmol, 1.24 g). The solutions were stirred and refluxed for 12 h. Yellow precipitate was filtered, washed by a small amount of methanol and dried in vacuum. yield 95%, mp 212–214 °C. Analyses for $C_{26}H_{20}N_2SO_3$; C, 70.90; H, 4.54; N, 6.36, Found C, 70.2; H, 4.4; N, 6.3. Main IR (KBr, cm−1): (C=N)1617, 1614 cm^{-1}

The advantages of synthesis procedure are: (1) the process is a simple involving one –step reaction with low cost materials : (2) the process is shorter: (3) methanol as solvent allows the formation of imine without for catalysis and (4) rapid reaction high and product can be isolated by filtration.

Extraction procedure:

Aqueous solutions containing 1.5×10^{-3} mol l^{-1} metal chloride or metal picrate [aqueous solution (10 ml) containing 1.25×10^{-5} M picric acid and 1×10^{-2} M metal nitrate] were placed in stoppered flask and shaken for 2 h at 25.0 ± 0.1 °C in appropriate buffer were equilibrated with equal volumes of the chloroform and nitrobenzene solutions of the Schiff base(4,4-diaminodiphenylsulfonbis (salicylideneamine) 4×10^{-4} mol l^{-1} by shaking in a mechanical shaker at 25 °C. Optimum equilibration time was determined for this system. In most cases distribution equilibrium was attained in less than 30 min and a shaking time of 120 min. The ionic strength of the aqueous was 0.1 M KCl in all experiments except those in which the effect of ionic strength was studied. After agitation, the solutions were allowed to stand for 120 min. The copper and chrome concentrations of the aqueous phase were determined by FAAS, and that of the organic phase from the difference by considering the mass balance. But the concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically at 355 nm. Blank experiments show that no picrate extraction The pH of aqueous phase was recorded as equilibrium pH.

The extractability of picrate (E%)was determined based on the absorbance of picrate ion in the aqueous.

$$\%E = \frac{A_0 - A}{A_0} \times 100$$

A_0 :absorption before extraction**.**

A :absorption after extraction

Results and discussion:

The preparation of ligands containing nitrogen and oxygen donor atoms are shown in Scheme 1. The structure of new compound was characterized by a combination of IR spectral data.

3.1. IR spectra

The IR spectra of the free ligands exhibit various bands in the region 250–4000 cm^{-1}. A full assignment of the IR spectra of Schiff bases is very difficult due to the extensive vibrational coupling in the molecules [21]. The observed bands in the ‘‘fingerprint’’ region are a result of strongly mixed vibrations. The main absorption bands are discussed with a comparison between the corresponding bands of compounds. The stretching frequency of the free ligand is expected in the 3300–3800 cm^{-1} region, however this frequency is shifted to 2595 cm^{-1}, for (I) and 2594 and 2589 cm^{-1} for (II) and (III) respectively. These bands are in a region due to the internal hydrogen bond OH ---- N-C . The band becomes broader and sometimes is not detected as the hydrogen bond becomes stronger. Hydrogen bonds in these Schiff bases are usually very strong. The ligands are relatively planar with adequate intramolecular distances that favor the formation of the hydrogen bond. Very strong bands near 1270 cm^{-1} have been assigned to in-plane bending vibrations of the ligands. We assign the strong bands at 1272 cm^{-1}(I), 1280 cm^{-1} (II) and 1282cm^{-1} (III) which are within the 1280–1340 cm^{-1} range reported for similar ligands. The C=N stretching frequencies are in the 1590–1650 cm^{-1} region as reported for similar ligands. The narrow bands near 1630 and 1580 cm^{-1} were observed in the region typical for the bands corresponding to the ν(C=N) coupled to the ν(C=C) vibrations , which suggested that the compounds are in the OH^- form (enol-imine form). The stretching frequency has been reported in the 1350–1410 cm^{-1} region. For the free ligands, the band occurring at 1394 cm^{-1} for (I) and at 1382 (II),(III) are assigned to the stretching frequency[22].

^{1}H and ^{13}C NMR spectra

The ^{1}H and ^{13}C NMR spectra of the Schiff bases, recorded in CDCl3 with the chemical shifts, expressed in ppm downfield from tetramethylsilane, are given in Figures (1-3). The NMR spectra of (I), (II) and (III) and ^{1}H NMR spectra of similar Schiff bases have been reported. (II) exhibits A broad peak at 13.91 ppm with an integration of 1.5 hydrogens and (II) at 8.44 ppm with 1.3 hydrogens. This peak is due to hydrogen bonded phenolic proton and the integration is less than 2.0 due to this intramolecular hydrogen bonding. The difference in the integration is probably due to the effects of the ethoxy group ortho to the phenol hydrogen. The signal for the hydrogen on the ArN=CHAr group, 8.33 ppm, is essentially the same for both Schiff bases. These peaks strongly indicate that the enol-imine tautomer is favored in chloroform solution. ^{1}H NMR data show that when the tautomeric equilibrium favors a enol-imine form singlets at 13.4 ppm, AOH, and ArCH=NAr at 8.5 ppm.

Extraction of metal ions with Schiff base

Effect of PH and solvents on the extraction of Cu(II) and Cr(III).

Various organic solvents as inert diluents were tested at a fixed pH containing equal amount of metal chloride and ligand solutions. The phase volume ratio was always maintained at 1:1 to avoid emulsion formation. The diluents, nitrobenzene and chloroform are same effective. The extract cause of this type of behavior is not known. The dielectric constant of medium has some contribution in the extraction process. However solubility parameter is only factor determining the extraction efficiency in the extraction process be taken into account and a better term correlating the relative extraction order [20].

The results indicate that H_2L in organic phase extracts efficiently Cu^{2+}, Cr^{3+} aqueous phase containing 0.1 mol L^{-1} KCl in the pH range of approximately 3-8.5 at 25°C.

In this research Liquid–liquid extraction experiments were performed to ex-amine the efficiency and selectivity of Schiff base in transferring metal ions (UO_2^{2+}) and d-metal ions (Hg^{2+}, Cu^{2+} and Cr^{3+}) from aqueous phase into chloroform. The results show that metals ions of UO_2^{2+} and Hg^{2+} are not extracted by Schiff base (E<1%).

The percentage extraction (%E) of metals into chloroform and nitrobenzene with Schiff base were plotted as a function of aqueous phase pH equilibrated with the organic phase in Fig. 7. The results are also expressed as distribution ratio (Table 1). The distribution ratio of cation may be represented by Eq. 1.

$$q = \frac{[MLA]_{org}}{[M^+]_{aq}} \qquad (1)$$

The degree of separation was determined in terms of 'separation factor' S_f defined as the ratio of q_1 for the desired metal ion M_1 to q_2 for the contaminant metal ion M_2.

$$S_f = \frac{q_1}{q_2} \qquad (2)$$

The selected relative cation seclectivity of Cu^{2+}/ Cr^{3+} was calculated from the distribution ratio of metal ion between the organic and aqueous phase as shown in Table 2.

The extractability and selectivity of cations were evaluated as a function of pH. The highest extractability and selectivity for Cu^{2+} in excess of cations such as Cr^{3+} was achieved at pH 6.2. The selectivity of Ligand to ratio Cu^{2+}/Cr^{3+} is equal to 58 for $CHCl_3$ and 41 for $C_6H_5NO_2$ (pH 6.2).

The extraction process may be represented by the equation:

$$M^{2+}_{(w)} + H_2L_{(0)} \leftrightarrow ML_{(0)} + 2H^+_{(w)} \qquad (3)$$

Where H_2L represents the extraction reagent and subscript (w) and (o) denote the aqueous and organic phases, respectively.

The extraction constant of the species(CuL, CrL) is given by.

$$K_{ext} = \frac{[CuL]_o[H^+]_w^n}{[Cu^{2+}]_w[H_nL]_o} \qquad (4)$$

When CuL is the only extractable species and the metal in the aqueous phase predominantly presented as cation Cu^{2+} . The metal distribution ratio (q) and the extraction constant are related by

$$Logq = LogK_{ext} + npH + Log[H_nL]_0 \qquad (5)$$

According to Eq (5) a plot of log q against pH at constant $[H_nL]$ at 4×10^{-4} M will give straight line

which slope is the number of hydrogen ions and intercept is log $[H_nL]$ + log K_{ext} (Fig. 8).

The effect of pH on the extraction of Cu^{2+} and Cr^{3+} ions from KCl media of ionic strenght (I=0.1 M) has been studied, the logarithm of the q values obtained were plotted against the corresponding pH values. A straight line with a slope of about 2 and 0.68 was obtained at I=0.1 of Cu^{2+} and Cr^{3+}, respectively, as shown Fig. 8. These values represent the number of hydrogen ions released during the formation of metal- ligand complex.

If the concentration of the extractant is constant and the hydrolysis in the aqueous phase as well as the polymerization in the organic phase occur to a negligible extent only, then the plots will be straight lines and their slopes will give the number of the ligands of the adducts.

Fig. 9 shows the evolution of log q when increasing the concentration of ligand at constant metal chloride concentration with two different organic solvents. As seen from the plots, there is a linear relationship between log q and log $[L]_{org}$, and the slope should be equal to the number of ligand molecules per cation in the extracted species. The slopes of lines are equal to 0.5 and 0.22 for Cu^{2+} and Cr^{3+}, respectively. Therefore, ligand forms a 2:1 (L:M) complex with Cu^{2+} and 3:1 (L:M) complex with Cr^{3+} for both solvents.

Conclusion:

The Schiff bases, was synthesized and characterized by elemental analysis, IR, mass spectrum, ^1H and ^{13}C NMR spectra. A comparison of the IR, , and ^1H and ^{13}C NMR spectra of Schiff base. For the both free ligands, the ν(C=N) and ν(C=N) could be assigned after deconvolution.

The Schiff base was synthesized, and the extraction of the metal ions were examined. The high transfer of Cu^{2+} and Cr^{3+} ions from the aqueous phase to the chloroform and nitrobenzene were observed with compound(H_2L), and results showed that the order of solvents is not change. Also The results show that metals ions of UO_2^{2+} and Hg^{2+} are not extracted by Schiff base.

The results indicate that H_2L in organic phase extracts efficiently Cu^{2+} and Cr^{3+} in aqueous phase containing 0.1 mol KCl in the pH range of approximately 5.5-8 and 6-8.2 respectively at 25°C.

Ligand gives the 2:1 and 3:1 complexes with Cu^{2+} and Cr^{3+} respectively for the both solvents.

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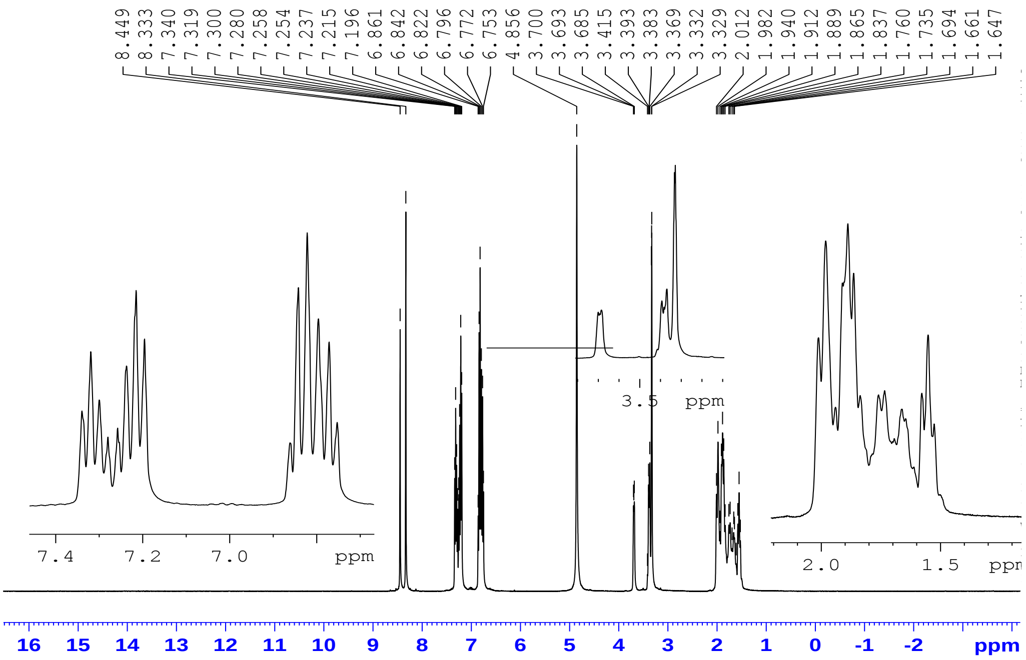

Fig. 1. ^{1}H spectra of Schiff base (I).

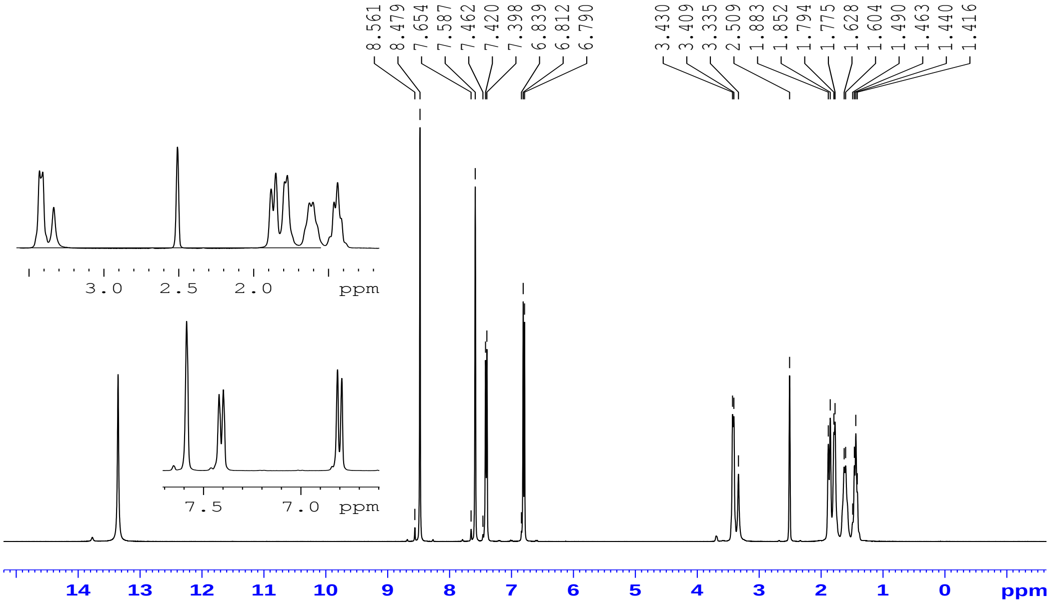

Fig. 2. ^{1}H spectra of Schiff base (II).

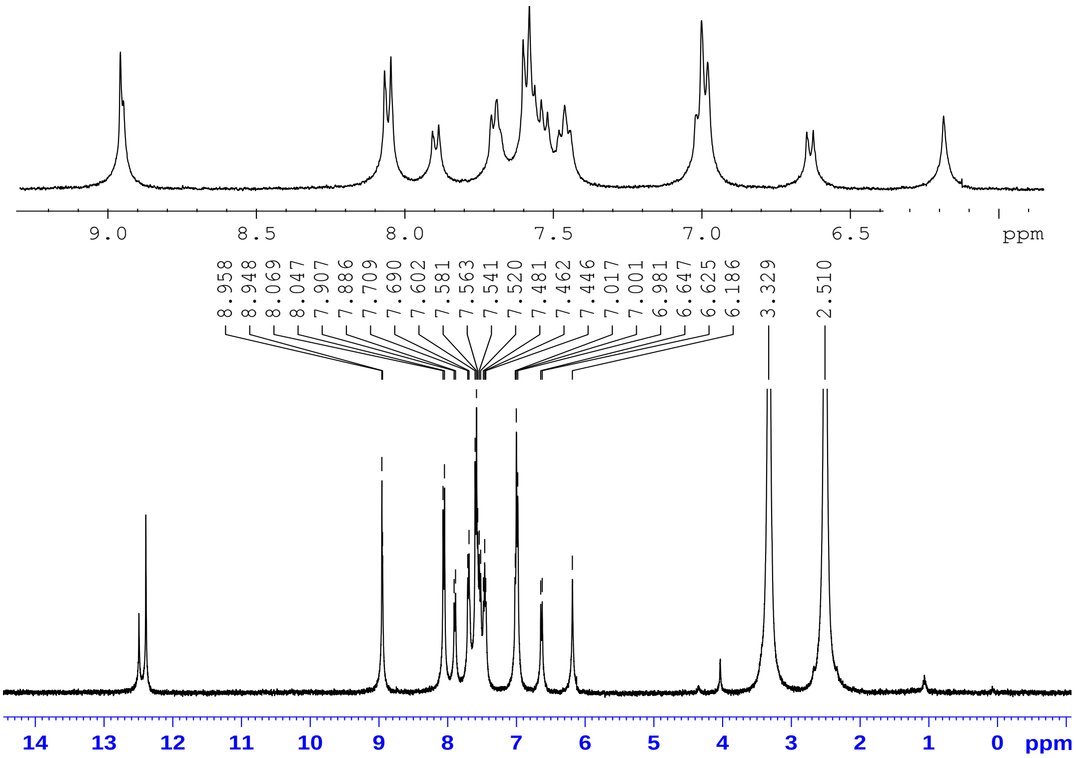

Fig. 3. ^{1}H spectra of Schiff base (III).

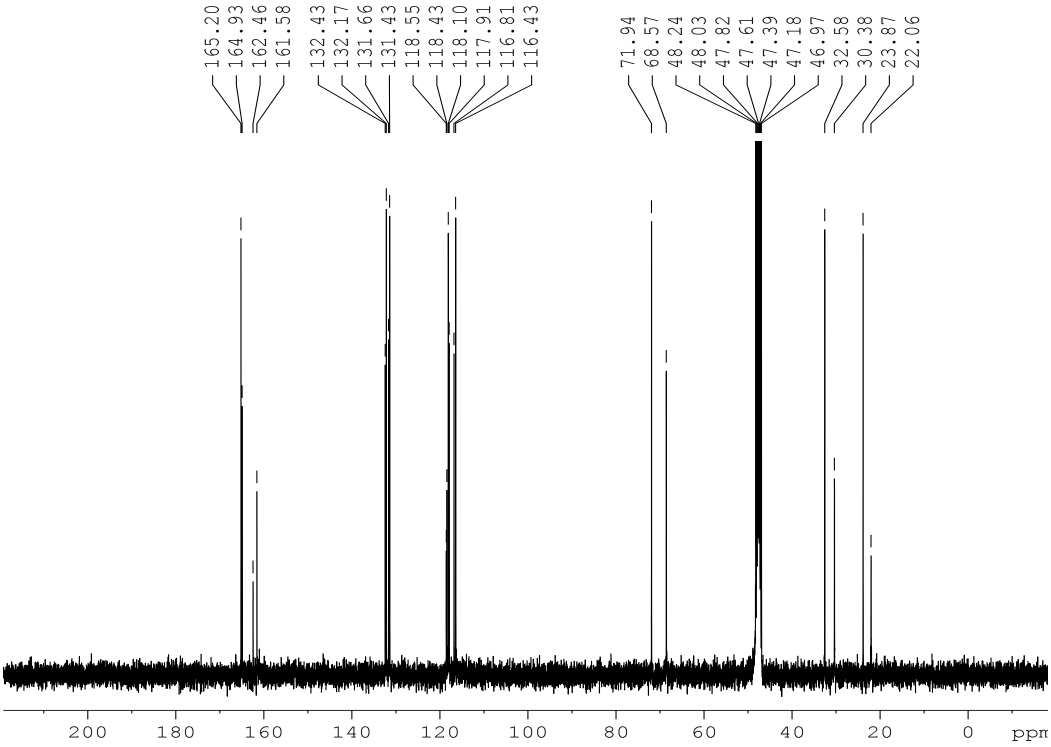

Fig. 4. ^{13}C NMR spectra of Schiff base (I).

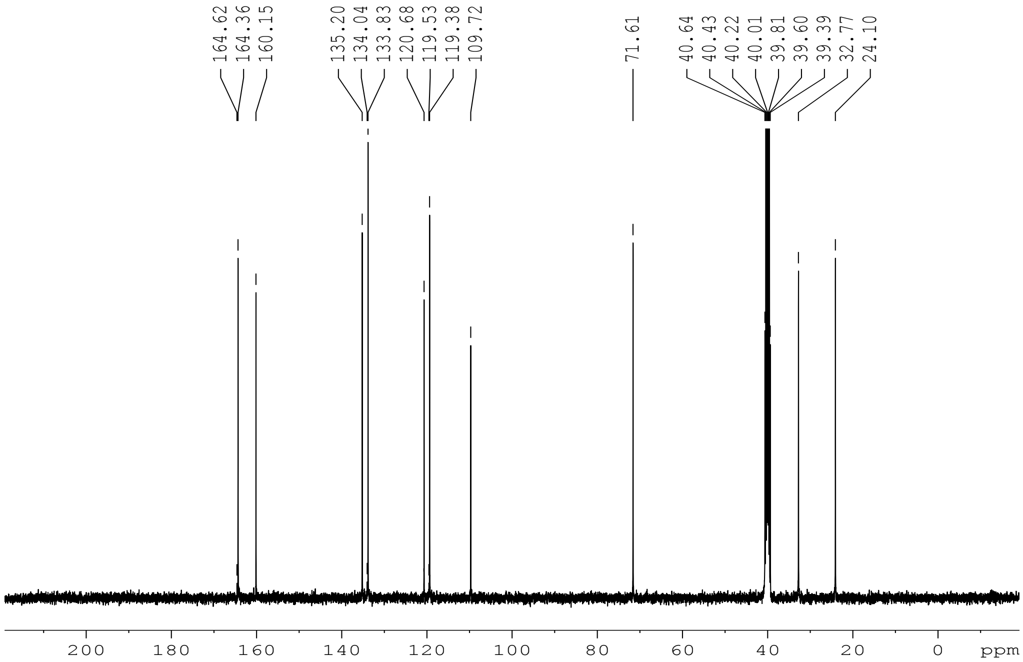

Fig. 5. ^{13}C NMR spectra of Schiff base (II).

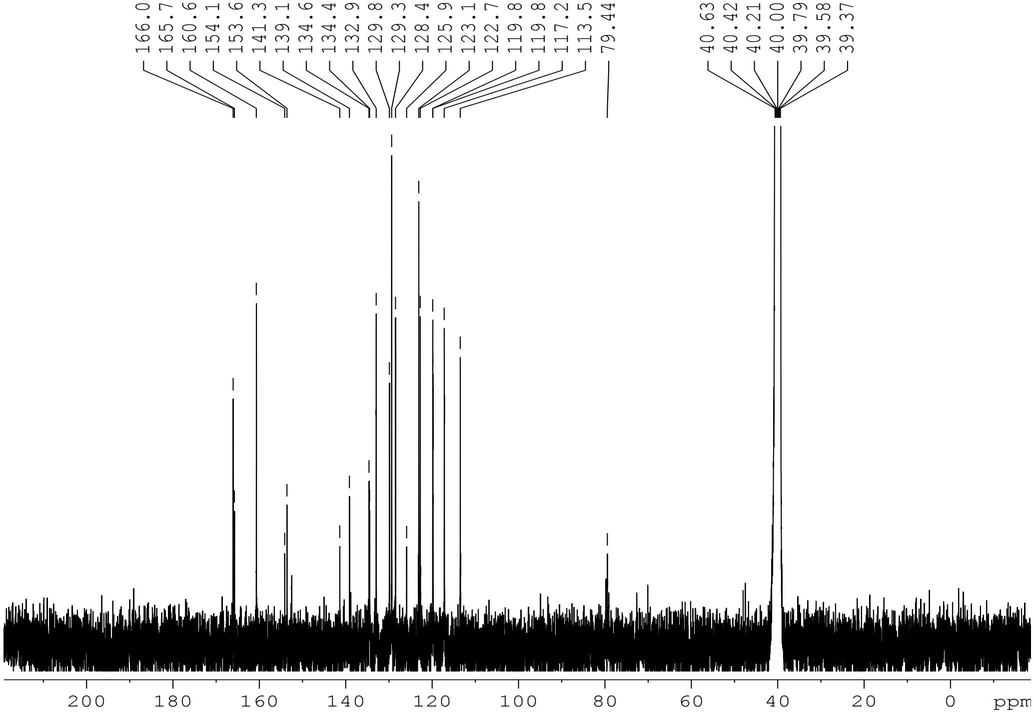

Fig. 6. ^{13}C NMR spectra of Schiff base (III).

Table 1. Distribution ratio of cation between organic and aqueous phases

pH	Distribution ratios of cations (D)[a]			
	Cu^{2+}		Cr^{3+}	
	Chloroform	Nitrobenzene	Chloroform	Nitrobenzene
3.27	0.07	0.08	0.52	0.80
4.12	0.24	0.02	0.75	0.78
5.08	0.24	0.2	0.83	0.70
6.27	67.7	43.85	1.26	1.00
7.05	36.29	30.5	12.62	4.79
7.57	20.86	35.68	9.4	6.6
8.15	20.45	18.21	4.7	4.8
8.4	23.22	21.18	1.4	5.7

[a] Averages calculated for data obtained from three independent extraction experiments

Table 2. The selected relative cation seletivities

pH	Selectivity (S_f)	
	Cu^{+2}/Cr^{+3a}	
	Chloroform	Nitrobenzene
6.2	58	41.5
7.05	3.5	7.51
7.57	3	3.68
8.15	4.1	3.98
8.4	14	1.8

[a] Relative cation selectivity determined by the distribution ratio of metal ion between organic and aqueous phases

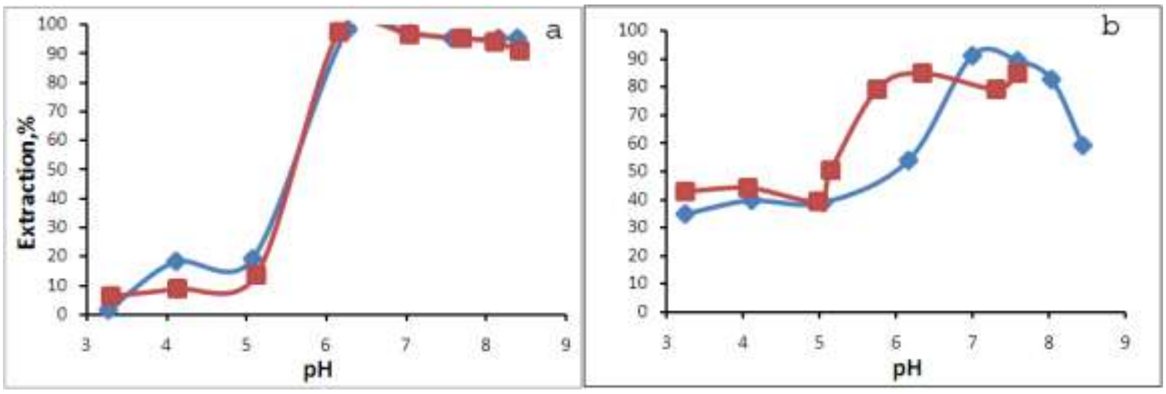

Fig. 7 Effect of pH and Solvents on the extraction of [a]Cr(III), [b]Cu(II).[🟦] $CHCl_3$, [🟥] $C_6H_5NO_2$.

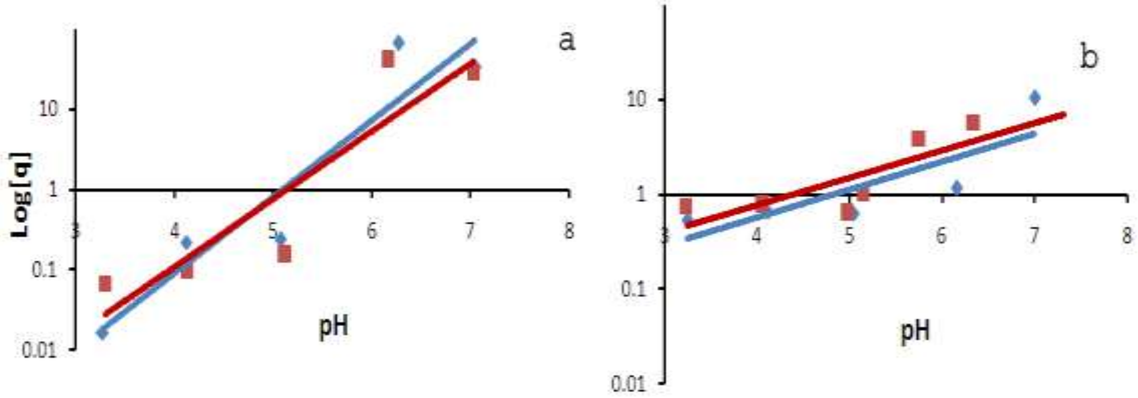

Fig. 8 The plot of log D vs. pH at Constant [H$_n$L] [a]Cu(II), [b]Cr(III).[🟦] CHCl$_3$, [🟥] C$_6$H$_5$NO$_2$

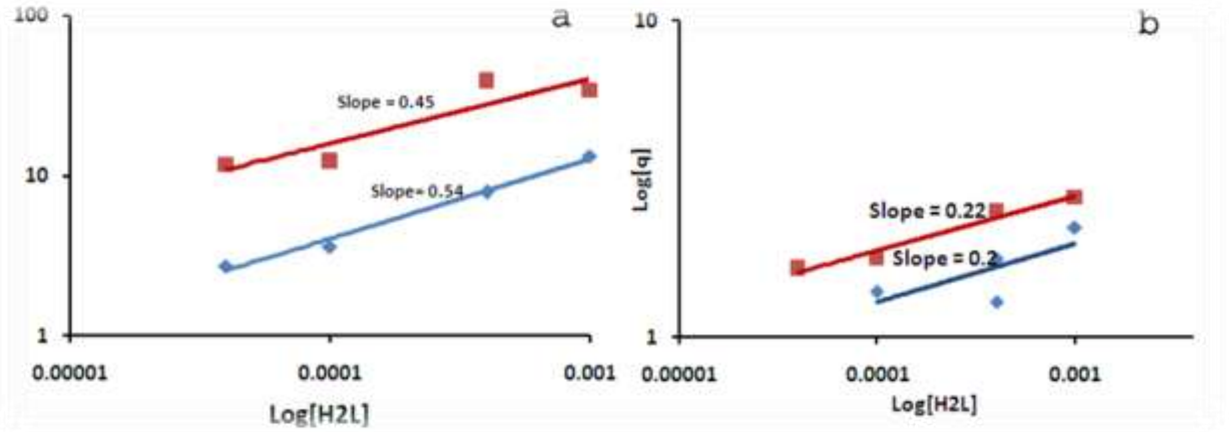

Fig. 9 The plot of log D vs. Log [H$_2$L] at Constant [H$_2$L] [a]Cu^{2+}, [b]Cr^{3+}.[🟦] CHCl$_3$, [🟥] C$_6$H$_5$NO$_2$