ISSN: 0067-2904
GIF: 0.851

Synthesis, Characterization and Stability Constant study of New Schiff Bases Derived from 2-Amino -2-deoxy Chitosamine and aldehydes with Some Metal Complexes

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Abstract

Two new Schiff bases (S_1,S_2) derived from 2-Amino-2-deoxy chitosamine and m-nitrobenzaldehyde (S_1), and with salicylaldehyde (S_2) were prepared and characterized using FTIR, UV and mass spectrometry. New complexes of the transition metal ions Co (II), Ni (II), Pd (II), Pt (II) with the two ligands were synthesized and their structures were elucidated depending on atomic absorption, FTIR, UV-visible spectra in addition to magnetic susceptibility and electrical conductivity measurement. Metal to ligand [M: L] ratio was obtained for all complexes in ethanol using molar ratio method, which gave comparable results with those obtained for the solid complexes. Stability constant of the complexes were determined using spectrophotometric method at 25^{o}C and ionic strength was maintained constants using 0.1M KNO_3.Stoichometry of the complexes by Job 's method showed that metal : ligand ratio is 1:1.

Keywords: Chitosamine, Schiff base, Metal Complexes, Glucosamine, Stability constant.

تحضير وتشخيص ودراسة ثوابت الاستقرارية لمعقدات قواعد شيف الجديدة المشتقة من 2-امينو-2- ثنائي اوكسي جيتوسامين والالديهايدات مع بعض المعقدات الفلزية

ندى مطير عباس*
قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

تم تحضيز اثنان من قواعد شيف الجديدة (S_1) مشتقة من 2-امينو – 2- ثنائي اوكسي جيتوسامين و ميتا نايتروبنزالديهايد و (S_2) مشتقه من 2-امينو – 2- ثنائي اوكسي جيتوسامين والسلسالديهايد. تم تشخيصها باستخدام تقنيات FTIR و UV وطيف الكتله كما تم تحضير سلسلة من المعقدات الجديدة لبعض ايونات فلزات العناصر الانتقالية مع S_1 و S_2 الجديدة مثل Co(II) وNi(II) وPd(II) وPt(II) وشخصت تراكيبها اعتمادا على نتائج تحاليل FTIR، UV-Vis، فضلا عن دراسة الصفات المغناطيسية والتوصيلية الكهربائية. اما نسبة الفلز: الليكاند (M:L) فقد تم الحصول عليها من دراسة كل المعقدات في الايثانول وباستخدام طريقة النسبة المولية والتي اعطت نتائج مقاربة للنتائج المستحصلة من دراسة المعقدات في الحالة الصلبة كما دُرست ثوابت الاستقرارية للمعقدات المحضرة باستخدام الطريقة الطيفية في 25^{o}م وتم حساب القوة الايونية باستخدام (0.1M KNO_3)، وباستخدام طريقة جوب وُجد ان نسبة الفلز:الليكاند مساوية الى 1:1.

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Introduction

Glucosamine ($C_6H_{13}NO_5$) (2-Amino-2-deoxy-glueose chitosamine) is an amino sugar and a prominent precursor in the biochemical synthesis of glycocylated proteins and lipids .Glucosamine is part of the structure of the polysaccharides chitosan and chitin, which compose the exoskelestone of crustaceans and other arthropods, cell walls in fungi and many higher organisms. Glucosamine is one of the most abundant monosaccharide [1]. It is produced commercially by the hydrolysis of crustacean exoskeletons, less commonly by fermentation of a grain such as corn or wheat [2]. In the US it is one of the most common non – vitamin, non – mineral, dietary supplements used by adults. One of the major application of chitosan and its derivatives is based on its ability to bind strongly heavy and toxic metal ions [3]. The stability constants of chitosan derivatives and their complexes with various transition metals have been determined previously [4]. This work presents the synthesis, characterization and bonding behavior with metal ions of two new Schiff base ligands prepared from the condensation reaction of glucosamine with m-nitrobenzaldehyde and salicylaldeyde.

Experimental

Reagents

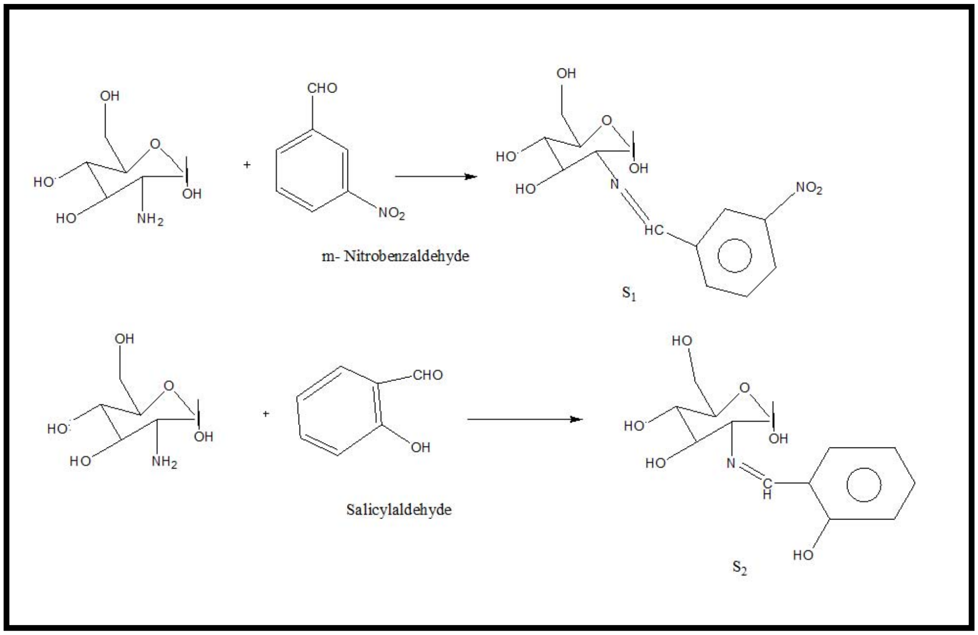
All chemicals used were of analytical reagent grade and Glucosamine Standard material was provided from the State Company for Drug Industries and medical appliances (SDI) Sammara - Iraq.

Apparatus

Melting Points were recorded on Gallenkamp melting point apparatus. The purity of the synthesized compounds was checked by TLC. Electronic spectra were obtained using ShimadzaUV- visible spectrophotometer at room temperature. FT-IR spectra were recorded using Shimadzu – 800 spectrophotometer in the range (4000 – 200) cm^{-1} and samples were measured as CsI disk. Mass spectra of the ligands were recorded on a JEOL SX 102/DA- 6000 mass spectrometer data system using argon, xenon (6kv, 10mA) as CI gas. Elemental microanalyses (C.H.N) were performed using a thermofinigan Flash. The metal contents of the complexes were determined by atomic absorption technique using z Varian- AA775. Molar conductivity measurements for complexes in DMF (10^{-3}M) at room temperature were carried out by using ELktaLictfahiskeit conductivity meter (SIE14ENS). Magnetic moments μ_{eff} (B.M) for the prepared complexes in the solid state were calculated according to Faraday's method using Johnson Mattey catalytic system division magnetic balance.

Synthesis of the ligands (S_1&S_2)

2-Salicylidene-2-deoxy-glucose-chitosamine (S_1) and 2-m-nitrobenzalidene-2-deoxy-glucose chitos-amine (S_2) were prepared by boiling equimolar amounts of the corresponding aldehydes (m-nitrobenzaldehyde (1.37g,0.01mol) and salicylaldehyde (1.22g,0.01mol) with 2-amino-2- deoxy- glucose chitosamine (1.79g,0.01mol), and (2-3) drops of glacial acetic acid in ethanol solution for 2hr. Upon cooling, a yellow crystalline (S_1), yellowish- orange (S_2) precipitates were formed .The products were filtered and then recrystallized from ethanol and diethyl ether [4]. Scheme (1) shows the synthesis routes of the two Schiff base ligands (S_1&S_2).



Scheme 1- Synthesis of S_1 and S_2

Synthesis of metal complexes

The metal complexes were prepared by mixing solutions of Schiff bases S_1 and S_2 (1.55g and 1.415g respectively, 5 mmol each)in ethanol and chloroform mixture(1:5) (40ml) with the metal salts: $CoCl_2.6H_2O$, $Ni(NO_3)_2.2H_2O$, $PdCl_2(PhCN)_2$ and $PtCl_2$ (1.18, 1.09, 1.8and 0.882 g respectively, 5 mmol each) and the mixtures were heated under reflux for ≈ 2h. The resulting solution was concentrated to a third its volume and cooled to (0^0C) for 6h. The precipitated complexes were filtered, washed with ethanol and dried over $CaCl_2$ [5,6]. The physical properties of the ligands and their complexes are shown in (Table -1).

Study of metal complex formation in solution

Stoichiometry and metal: ligand ratios of metal complexes with the two Schiff base ligands were determined in ethanol following Job's method by plotting the absorbance versus mole fraction at fixed wavelength of maximum absorption [6]. Fresh stock solutions of the two Schiff base ligands (S_1&S_2, $6x10^{2-}M$) were prepared by dissolving the accurately weighed amount of ligands (0.0186, 0.0162 g/l respectively) in ethanol .

Fresh stock solution of metal salts ($6x10^{2-}M$) were prepared by dissolving the accurate amount of metal salt (Co^{2+},0.014g/L, Ni^{2+},0.013g/L , Pd^{2+}, 0.022 g/L, Pt^{2+} ,0.011g/L,) in appropriate volume of solvent.

Table (1) Molecular formula, physical properties and atomic absorption of metal complexes of S_1 and S_2

Symbol Molecular formula	Color	M.P.C° (dec.)	Yield %	Elemental Analyses% found (calculated)			
				C	H	N	M
$S_1(C_{13}H_{15}O_7N_2)$	Yellow	82	67	50.90 (50.16)	4.22 (4.82)	9.32 (9.00)	/
$C_1[(C_{13}H_{15}O_7N_2)CoCl_2].H_2O$	Violet	179	53	43.18 (43.06)	3.82 (3.27)	6.51 (6.114)	12.3 (12.868)
$C_2[(C_{13}H_{15}O_7N_2)Ni(ONO_2)_2]$	Dark green	185	62	31.93 (31.598)	3.32 (3.083)	11.10 (11.34)	10.90 (11.8)
$C_3[(C_{13}H_{15}O_7N_2)PdCl_2]$	Greenish brown	192	43	32.61 (32.00)	3.32 (3.077)	5.21 (5.77)	21.39 (21.833)
$C_4[(C_{13}H_{15}O_7N_2) PtCl_2]$	Dark brown	188	47	27.92 (27.046)	2.82 (2.77)	4.25 (4.86)	33.62 (33.86)
$S_2 (C_{13}H_{17}O_6N)$	yellowish-orange	76	58	55.67 (55.12)	6.17 (6.00)	4.25 (4.94)	/
$C_5[(C_{13}H_{17}O_6N)Co Cl] Cl.H_2o$	green	142	36	35.67 (36.369)	3.49 (3.73)	3.25 (3.26)	13.00 (13.73)
$C_6[(C_{13}H_{17}O_6N) Ni (ONO_2)]NO_3 2H_2O$	Bluish green	130	58	36.20 (31.157)	3.52 (3.195)	3.72 (2.796)	11.68 (11.72)
$C_7[(C_{13}H_{17}O_6 N) PdCl_2]$	Brown	210 dec.	60	33.37 (33.95)	3.29 (3.70)	3.92 (3.05)	23.62 (23.16)
$C_8[(C_{13}H_{17}O_6N_1) PtCl_2]$	Light brown	230 dec.	48	28.83 (28.37)	3.32 (3.09)	2.94 (2.54)	35.02 (35.48)

Results and discussion

The mass spectra of the two Schiff bases (S_1 & S_2) are shown in figures (1,2). The CI mode mass spectrum of S_1 & S_2 gave a peaks m/z = 313,282 which were assigned to [M+1] and displayed peaks corresponding to [M+] fragments at (312, 283) molecular ions for S_1 & S_2 respectively. Both ligands showed peaks at m/z 179, 111, 68 which are characteristic of many glucosamine derivatives [4-6]. The results of elemental analyses (CHN), metal contents, and some physical properties of prepared compounds are described in (Table -1).

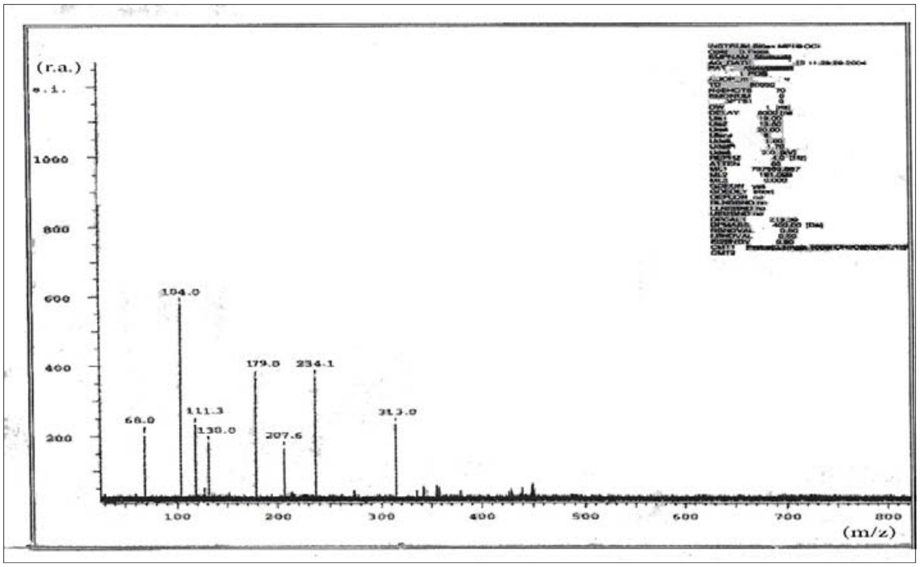


Figure 1- Mass Spectrum of S_1

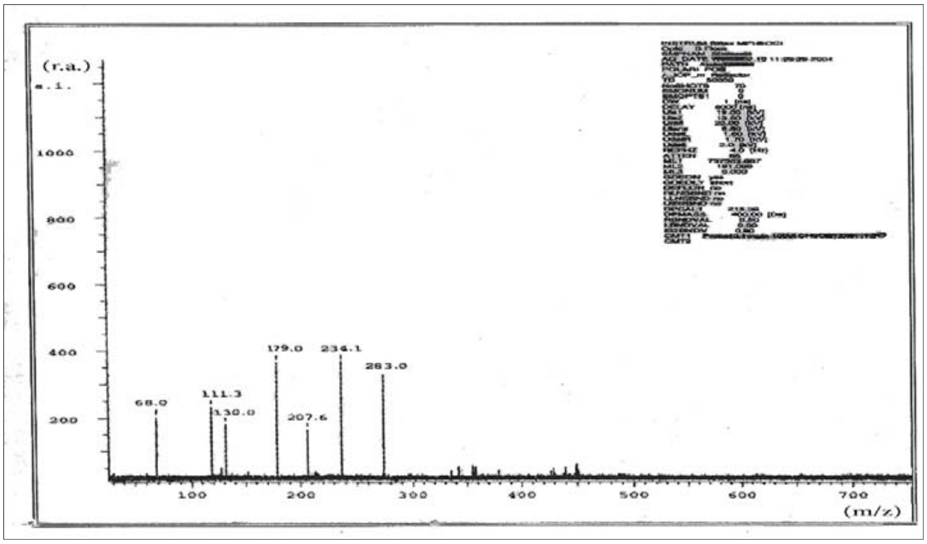


Figure 2- Mass Spectrum of S_2

The results obtained are in good agreement with those calculated for the suggested formula. The FTIR data of S_1 and S_2 and their complexes are presented in (Table -2). The FTIR spectra of S_1 and S_2 exhibited the absence of bands attributed to (ν_{NH2}) of chitosamine [7,8].The (OH) stretching mode of both S_1&S_2 appeared as a broad medium intensity band ~2900 cm^{-1} assignable to hydrogen bond[9].The band observed at 2950 cm^{-1} was assigned to stretching mods of (C-H) band. The two bands observed at 1631 and 1626 cm^{-1} were assigned to ($_{C=N}$) vibrations of azomethine group for the two ligands respectively[10] which support the formation of Schiff base ligands figures -(3,4). Metal complexes of S_1&S_2 showed shifts to lower frequencies in (ν_{OH}) for all complexes, which refer to coordination with metal ions [11]. The stretching vibrations of ($\nu_{C=N}$) in all complexes were shifted to lower frequencies. These shifts refer to the coordination of azomethine group with metal ions. Bands related to lattice water were observed in the spectra of C_1, C_5 and C_6 [11, 12].The nitrate group of Ni (II) complexes (C_2 and C_6) exhibited as monodentate behavior. New bands appeared at lower frequencies and were assigned to M-N, M-O and M-Cl stretching modes [12]. The electronic spectra of S_1 and S_2 in ethanol exhibited a sharp high intensity band appeared at 33011 cm- which were assigned to (π---π^*) of conjugated system [13,14]. All complexes exhibited changes in profile and position of ligands bands. The spectra of Co(II) complexes showed a single band assigned to transition $^4A_2g \rightarrow {}^4T_1g(F)(\nu_2)$ and a multiple band assigned to $^4A_2g \rightarrow {}^4T_1g(P)(\nu_3)$ .The magnetic moment values were (4.132-4.65BM) and this refers to tetrahedral geometry around the Co(II) ions[15,16]. The Ni(II) complexes exhibited bands assigned ${}^3T_1g(F) \rightarrow {}^3A_2g(F)(\nu_2)$and ${}^3T_1g(F) \rightarrow {}^3T_1g(P)(\nu_3)$[17].These data together with the magnetic moment values (2.803-2.735BM) for C_2 and C_6 respectively refer to tetrahedral geometry around Ni(II) ions[18].The observed band energy of Co(II) and Ni(II) complexes of both ligands were applied on Tanaba-Saugano diagrams of the two ions to obtain the values of the interelectronic repulsion parameter B-, nephelauxetic ratio (β), Dq/B- as well as calculate the values of 10Dq [19a,b]. The spectrum of diamagnetic Pd(II) complexes (C_3 and C_7), showed two bands assigned to ${}^1A_1g \rightarrow {}^1A_2g$ (ν_1) and ${}^1A_1g \rightarrow {}^1B_1g(\nu_2)$ of square planar Pd(II) complexes[20].The spectrum of diamagnetic Pt(II) complexes (C_4 and C_8) exhibited two absorption bands which were assigned to ${}^1A_1g \rightarrow {}^1Eg$ and ${}^1A_1g \rightarrow {}^1E_2g$ of square planar Pt(II) complexes[20,21]. A charge transfer band was also observed in the spectrum of C_8 [21]. Ionic properties of the complexes were estimated from conductivity measurement in DMF solution [22, 23] and are described in (Table-3). All complexes were nonionic except C_5 and C_6 which have electrolytic nature of 1:1. According to the above mentioned data and those of elemental analyses and i.r. spectra, the structures of the metal complexes can be suggested as illustrated in (scheme-2).

Table (2) Characteristic I.R. vibrations (cm^{-1}) for S_1 & S_2 and their Metal Complexes

Comp. No.	**Infrared (cm^{-1})**							
	ν_{OH} (hydroxyl group)	**$\nu_{C=N}$**	**$\nu_{C=C}$ aromatic ring**		**ν_{C-O} phenolic**	**ν_{M-X}**		
						M-O	**M-N**	**M-Cl**
S_1	2900,3450	1631	1581	1498	1277			
C_1	3406	1611	1541	1500	1296	465	383	318
C_2	3320	1618	-	1527	1296	472	327	332
C_3	3420	1615	1540	1523	1283	570	427	360
C_4	3410	1620	1542	1518	1290	582	470	329
S_2	3423	1626	1547	1517	1315	-		-
C_5	3417	1622	1539	1512	1306	468	300	313
C_6	3410	1607	1541	1518	1307	468	490	310
C_7	3409	1610	1544	1520	1292	552	410	302
C_8	3408	1613	1550	1523	1293	490	325	371

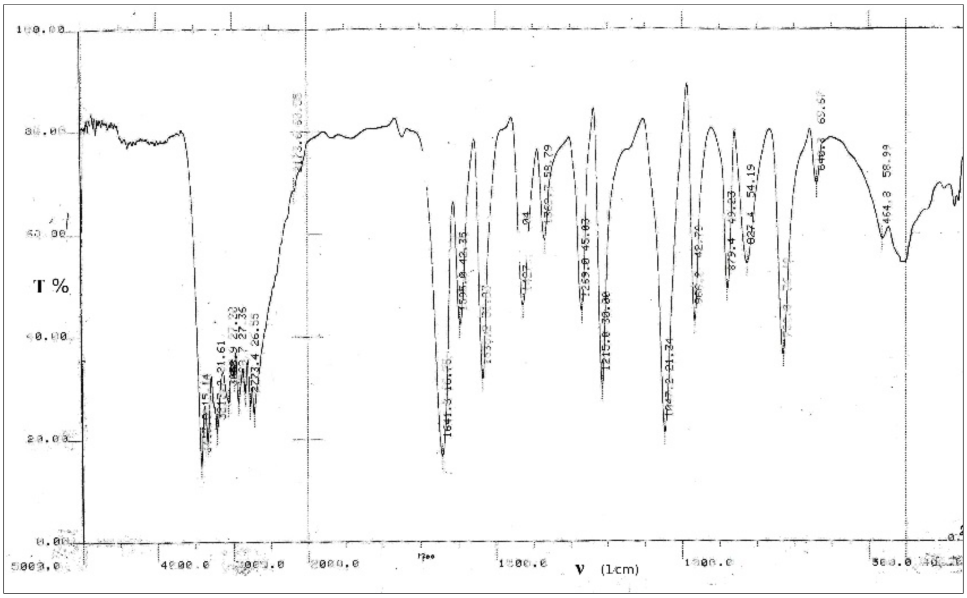


Figure 3- Infrared spectrum of S_1

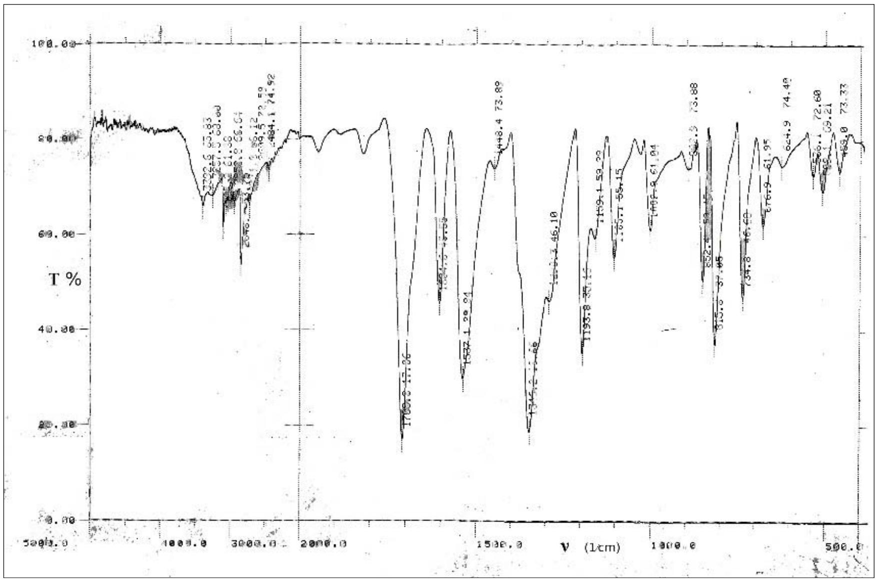
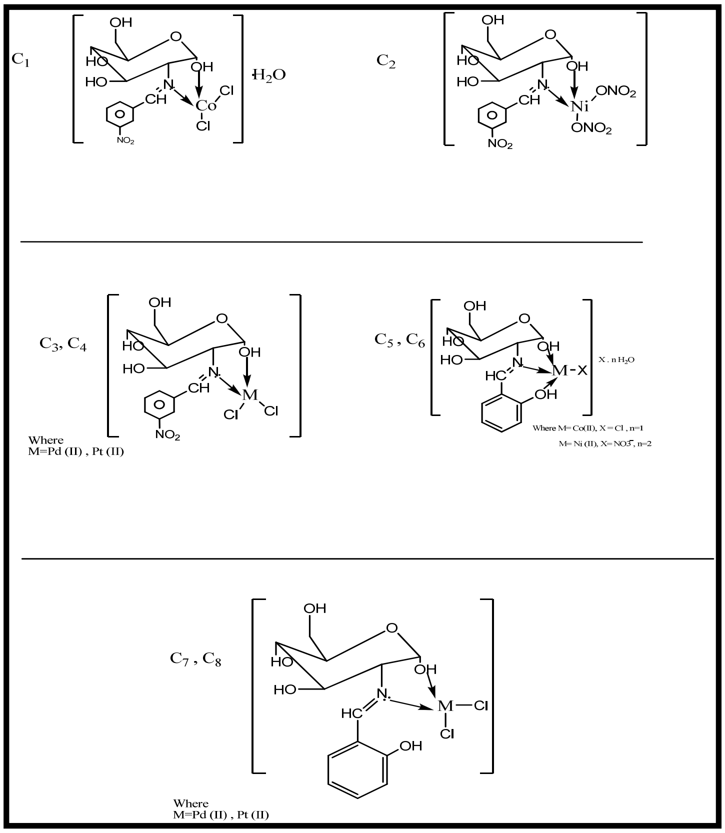


Figure 4-Infrared spectrum of S_2

Table 3- Electronic Spectra Parameters, molar conductivity and effective magnetic moments (μ_{eff}) of Schiff bases complexes

Comp. no	Band position (cm^{-1})	Assignment	Dq /B$^-$ (cm^{-1})	β	10Dq cm^{-1}	Ω (s.mol.cm^2)	μ_{eff} (BM)	Suggested Structure
C_1 Co(II)	ν_1 7389 (cal.) ν_2 9234 ν_3 15259	$^4A_{2g}\rightarrow{}^4T_{2g}$ (F) $^4A_{2g}\rightarrow{}^4T_{1g}$ (F) $^4A_{2g}\rightarrow{}^4T_{1g}$ (P)	1.52	0.42	7587	12.0	4.65	Tetrahedral
C_2 Ni (II)	ν_1 5050 ν_2 10124 ν_3 18125	$^3T_{1g}$ (F)$\rightarrow{}^3T_{2g}$ (F) $^3T_{1g}$ (F)$\rightarrow{}^3A_{2g}$ (F) $^3T_{1g}$ (F)$\rightarrow{}^3T_{1g}$ (P)	1.4	0.51	4930	10.0	2.803	Tetrahedral
C_3 Pd (II)	ν_1 16176 ν_2 130157	$^1A_{1g}\rightarrow{}^1A_{2g}$ $A_{1g}\rightarrow B_{1g}$	-	-	-	7.0	Diamag.	Sq. Planer
C_4 Pt (II)	$\nu_1$178601 ν_2 20450 $\nu_3$29851	$^1A_{1g}\rightarrow{}^1E_g$ $^1A_{1g}\rightarrow{}^1E_{2g}$ $^1A_{1g}\rightarrow{}^1B_{1g}$	-	-	-	6.4	Diamag.	Sq. Planer
C_5 Co (II)	$\nu_1$6084 cal $\nu_2$1010 $\nu_3$15778	$^4A_{2g}\rightarrow{}^4T_{2g}$ (F) $^4A_{2g}\rightarrow{}^4T_{1g}$ (F) $^4A_{2g}\rightarrow{}^4T_{2g}$ (P)	1.22	0.477	5098	121.3(ionic)	4.132	Tetrahedral
C_6 Ni (II)	$\nu_1$7250 $\nu_2$11930 $\nu_3$15800	$^3T_{1g}$(F)$\rightarrow{}^3T_{2g}$(F) $^3T_{1g}$(F)$\rightarrow{}^3A_{2g}$ (F) $^3T_{1g}$(F)$\rightarrow{}^3T_{1g}$ (p)	1.2	0.62	7065	137.1(ionic)	2.735	Tetrahedral
C_7 Pd(II)	ν_1 15915 ν_2 20638 26223	$^1A_{1g}\rightarrow{}^1A_{2g}$ $^1A_{1g}\rightarrow{}^1B_{1g}$ $^1A_{1g}\rightarrow{}^1E_g$	-	-	-	9.8	Diamag.	Sq. Planer
C_8 Pt (II)	$\nu_1$16952 $\nu_2$19420 $\nu_3$24063	$^1A_{1g}\rightarrow{}^1A_{2g}$ $^1A_{1g}\rightarrow{}^1E_g$ (C.T)	-	-	-	13.2	Diamag.	Sq. Planer



Scheme 2- Suggested Structures of S_1 and S_2 metal Complexes

Stability constants of Schiff base complexes:

Determination of the (λ_{max}) of the metal-ligand solution

A number of solutions were made by mixing different volumes of 9.00 x 10-3 M solution of each metal salt and 9.00 x 10-3M of standard solution of each ligand [24] in ethanol solution of 0.1M KNO3 .The pH was adjusted to 7.5 , at room temperature. The absorbance was scanned in the range 200-1100 nm to determine (λ max) for each complex which are shown in (Table- 4). The results obtained from Job's plot showed that (Metal:S1), and (Metal:S2) ratio were (1:1).

Table 4- Stability constant data for the studied metal-ligand systems in ethanolic solution of 0.1M KNO3

Ligand	Metal ion	λ max	Metal = Ligand	Stability constant (Log β^-)
S_1	Co (II)	642	1 = 1	10.93
	Ni (II)	655	1 = 1	11.32
	Pd (II)	642	1 = 1	9.84
	Pt (II)	650	1 = 1	8.96
S_2	Co (II)	503	1 = 1	5.87
	Ni (II)	644	1 = 1	6.29
	Pd (II)	655	1 = 1	5.34
	Pt (II)	542	1 = 1	5.28

The stability constants of metal ions(Co^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}) with the two Schiff base ligands were determined spectrophotometrically using the modified procedure of Hilderbrand and Benesi [24-26]. A series of seven solutions were prepared with a constant concentration of metal ion[M_0] and variable ligand concentration [L_0] in ethanolic solution of (0.1 M KNO_3**) a**t pH 7.5. The reaction mixture was stirred continuously and allowed to stand for 15 minutes. The progress of reaction was monitored spectrophotometrically by recording absorbance of each mixture at (λ max) .The stability constant, β^- was determined using Hilderbrand and Benesi equation [26,27].

$M_0/ A= 1/\beta^- \varepsilon_c [1/L_0] + 1/ \varepsilon_c$ where

M_0=constant concentration of metal ion at pH=7.4.

L_0 =variable concentration of ligand at pH=7.4 .

β^- =stability constant and A= absorbance.

Plot of M_0/A versus $1/L_0$ (Figures -(5&6)) for complexes of S_1 and S_2 respectively gives the $1/\varepsilon_c$ and slope is $1/\beta^- \varepsilon_c$. The plot of this equation (M/A vs. $1/L_0$) showed linear relationships between the two variables. From the values of β^- (Table-4), the stability of complexes were evaluated.

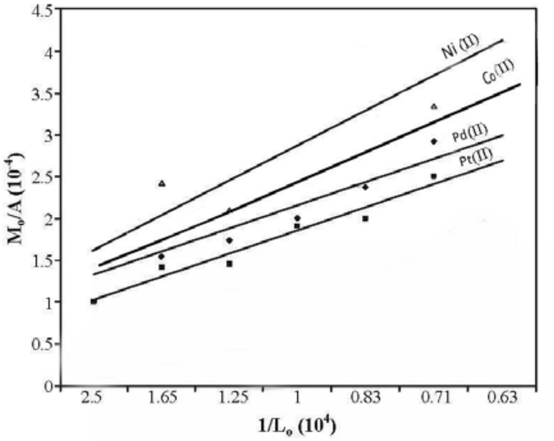


Figure 5-Plot of stability constant data of interaction of metal ions withS_1.

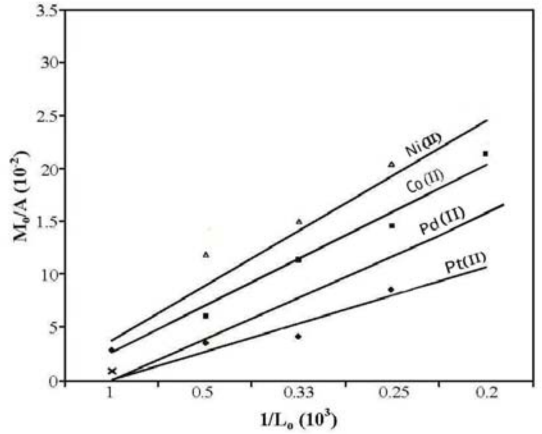


Figure 6- Plot of stability constant data of interaction of metal ions with S_2.

The stability constants were inversely proportional to the ionic radii of metals. The order of stability constants and reactivity of the ligands toward metal ions followed the trend Pt (II)<Pd(II)< Co(II)< Ni(II). The order indicates that (β^-) values increases with decreasing ionic radius of the metals. The data also reveals that the Ni^{2+} ions formed more stable complexes with (S_1&S_2) ligands compared to other metal ions .This may be explained on the basis of differences in the charge/size of the metal ions. Which allows for closer approach of ligand molecules and better electrostatic attraction with the metal ion [28]. The effect of basicity of the ligand and charge /size ratio on metals on stability constants (β^-) are emphasized. Comparison between stability constants of Co(II),Ni(II), Pd(II) and Pt(II) complexes of ($S_1$and S_2) shows that complexes of S_1 are more stable than those of S_2 [29].

Conclusion

The present work included the preparation of a new group of Schiff base type exhibiting bidentate chelating behavior with different metal ions. The stability constants of the complexes were evaluated by applying the method of Hilderbrand-Benesi . The highest stability constants were exhibited by the Ni (II) complexes which reflects the higher affinity of these ligands toward nickel (II) compared with the remaining metal ions.

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