



## Preparation and Characterization of New Metal Complexes of Schiff Bases Containing a Thiazole Ring

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### Abstract

New metal Complexes of two newly prepared Schiff bases ( $L_I$  and  $L_V$ ) and three previously prepared Schiff bases  $HL_{II}$ ,  $L_{III}$ ,  $L_{IV}$  by reacting 2-amino benzothiazole(2-ABT) with 2,4-dimethoxybenzaldehyde, salicylaldehyde, 4-hydroxy benzaldehyde, N,N-dimethyl-4-aminobenzaldehyde and from reaction of 2-aminothiazole (2-AT) with 2,4-dimethoxy benzaldehyde respectively. Structures were proposed depending on elemental and thermal analyses (TG and DTG) and by i.r and u.v- visible spectra in addition to magnetic susceptibility and electrical conductivity measurements. Some of these compounds exhibited growth inhibition against two types of bacteria.

### الخلاصة

حضرت معقدات فلزية جديدة لاثنتين من قواعد شيف جديدة  $L_I$  و  $L_V$  وثلاثة من قواعد شيف محضرة سابقاً  $HL_{II}$  و  $L_{III}$  و  $L_{IV}$  من مفاعلة 2-امينوبنزوثيازول مع كل من 2, 4 - ثنائي ميثوكسي بنزالددهايد وساليسيل الديهيد و 4- هيدروكسي بنزالددهايد. و N, N - ثنائي ميثيل بارا امينو بنزالددهايد ومن مفاعلة 2- امينو ثيازول مع 2, 4 - ثنائي ميثوكسي بنزالددهايد على التوالي. شخّصت التراكيب الكيميائية بواسطة التحليل الدقيق للعناصر والتحليل الحرارية TG, DTG, ونتائج اطراف الاشعة تحت الحمراء والاشعة فوق البنفسجية- المرئية فضلاً عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية للمعقدات الفلزية. اظهرت بعض المركبات المحضرة قابلية على تثبيط نمو نوعين من البكتريا المرضية

### Introduction

Schiff bases derived from aromatic aldehydes containing-  $OCH_3$ , OH or halogen groups were reported to have higher antifungal activity than those of unsubstituted aromatic rings (1,2). In industry, these derivatives were used as anticorrosion agents and as fixing agents for fabric printing (3).

The importance of Schiff bases complexes were described in the literature (4,7). They were used as synthetic models for the explanation of biological reactions mediated by active metal centers such as oxygen carriers (hemocyanine, hemoglobin, myoglobin(6,7)) and in electron

transfer reactions (4,5,7). Furthermore some complexes of Schiff bases were found more active than parent ligands against bacteria and fungi (8,9), herbicides, and anticancer agents(10). In this work a new series of transition metal complexes of two new Schiff bases was prepared and studied. New complexes of three previously prepared Schiff bases(11,13) , derived from condensation of 2- aminobenzothiazole (2-ABT) and 2- aminothiazole (2-AT) with different aromatic aldehydes were also prepared and studied. The structural formula of these compounds are illustrated in Scheme (1) and names are described in table (1).

**Experimental****Apparatus:**

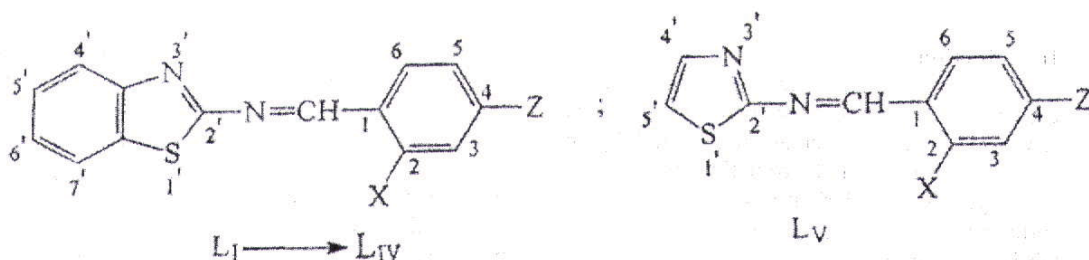
Melting points (uncorrected) were obtained using Gallenkamp MF 600-010F melting point apparatus. Elemental analyses were performed by using Elemental analysis – Perkin Elmer 240B and Elemental analysis model CHNSO-Carlo-Erba instruments. Infrared spectra of ligands and complexes were recorded as KBr and CsI discs respectively on Perkin- Elmer 983 GIP and Pyeunicam sp-300 i.r spectrophotometer. Electronic spectra of ligands in ethanol and complexes in DMF were recorded on u.v- visible spectrophotometer Shimadzu u.v- 160A. H.n.m.r Spectra of ligands in DMSO were recorded on Hitachi- Perkin- Elmer spectrophotometer at 60 MHz with TMS as a reference.. Thermal analyses by TG and DTG were obtained by using Stanton Redcorft TG 760 series and thermogravimetric Analyzer (TGA) A Du-pont Thermobalance Model 951. Electrical conductivity of metal complexes in DMF ( $10^{-3}$ M) were measured at room temperature by using Capacitor Analyzer and Resistance Bridge type CRB3. Magnetic susceptibilities ( $\mu_{\text{eff}}$  B.M) of metal complexes in the solid states were measured at room temperature by Faraday method using Bruker Magnet B.M.6. Determination of metal content (%) of complexes were carried out by using Shimadzu-680G atomic absorption of flame emission spectrophotometer and Elemental analyser MOD 1106 Carlo-Erba.

**Materials and Methods**

Metal salts  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , 98%,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  38%,  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (Purum),  $\text{PdCl}_2$ , 60% (Fluka),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . (extra pure) (Merck), were used as received from suppliers. N, N-Dimethyl – 4- amino benzaldehyde, 99% benzonitrile (puriss) (Fluka), and triethyl amine 99.5% (BDH) were used without further purification. Dimethyl formamide and ethanol were dried before distillation (14,15). 2-Amino benzothiazole (2-ABT) was purified by crystallization from boiling water (16) and 2-aminothiazole was purified by sublimation under reduced pressure. 4-Hydroxy benzaldehyde 99% was purified according to a method mentioned in the literature (15). The preparation of 2- chlorobenzonitrile palladium (II) was carried out according to a reported method (17). The purity of all products were confirmed by T.L.C. using silica gel and different ratios of chloroform and acetone mixture as eluents.

**Preparation of Schiff bases**

The ligands  $L_I$ - $L_V$  described in table (1) and illustrated by structures (a) and (b) in scheme –1- were prepared by adding ethanolic solutions (0.01 mole) of the amine to (0.01 mole) of aldehyde in dry ethanol. The amount of solvent should be as minimum as possible. 3-4 drops of piperidine were added and the solution was heated under reflux on a water bath for 30 min. with continuous stirring. A precipitate was formed after cooling the mixture to room temperature. The product was filtered off, washed with cold ethanol and ether and crystallized from ethanol then dried under vacuum.



Scheme (1):-Schiff bases derived from 2-amino thiazole and 2-amino benzothiazole

Table (1): Schiff bases derived from thiazoles and aromatic aldehydes

Symbol	Nomenclature	X	Z
L <sub>I</sub>	N-(2,4- Dimethoxy benzylidene) benzothiazole	OCH <sub>3</sub>	OCH <sub>3</sub>
HL <sub>II</sub>	N- (Salicylidene)- benzothiazole	OH	H
L <sub>III</sub>	N- (4-Hydroxy benzylidene) benzothiazole	H	OH
L <sub>IV</sub>	N-(4-N,N-Dimethylaminobenzylidene)- benzothiazole	H	(CH <sub>3</sub> ) <sub>2</sub> N
L <sub>V</sub>	N- (2,4- Dimethoxy benzylidene)- thiazole	OCH <sub>3</sub>	OCH <sub>3</sub>

### Preparation of metal complexes

An ethanolic solution of metal salt (1 mmole) was added to an ethanolic solution of ligand (2 mmole) with continuous stirring. In case of C<sub>4</sub> and C<sub>5</sub> (2 mmole) of Et<sub>3</sub>N were added. Precipitation took place immediately. Each mixture was then heated under reflux for 30 min to allow complete precipitation. The products were filtered off, washed with ethanol, followed by ether and dried under vacuum.

### Results and Discussions

#### a) Physical data and elemental analyses:

Table (2) describes the physical properties of ligands and complexes together with CHN analyses and atomic absorption. The suggested molecular formulae were further supported by

thermal analyses and spectral studies. Elemental analyses of some complexes recorded deviation in hydrogen content (especially C<sub>7</sub>, C<sub>8</sub> and C<sub>11</sub>) because of technical errors in the instrument.

#### b) H.M.R. Spectra:

The N.M.R. spectrum of L<sub>I</sub> in DMSO gave the following chemical shifts  $\delta$ (ppm): 2.85 (s, 3H, OCH<sub>3</sub>), <sup>(18)</sup> 2.95 (s, 3H, OCH<sub>3</sub>) <sup>(18)</sup>; 6.3-6.5 (m, 4H<sub>A</sub>, aromatic H<sub>A</sub>) <sup>(18)</sup>; 6.7-7.0 (m, 3H<sub>B</sub> o,p-trisubstituted benzene) <sup>(18)</sup>; 8.15-8.3 (s, 1H, CH for schiff base) <sup>(19,20)</sup>. Additional chemical shifts were observed and were assigned to lattice ethanol <sup>(18)</sup>. 1.4-1.6 t (CH<sub>3</sub>); 2.2 -2.5 g (CH<sub>2</sub>); 5.6-2.75 (OH) and 3.2-3.4 for DMSO <sup>(21)</sup>.

Table (2): Molecular formula, Physical properties, and elemental analyses (%) of Schiff bases and their metal complexes.

Symble Molecular formula (Colour)	(m.p)°C Yield %	Elemental analysis % found (calculated)			M% Found (Calculated)
		C%	H%	N%	
L <sub>I</sub> [C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> SO <sub>2</sub> ].0.5 EtOH(yellow)	(135-137) 70%	61.7 (61.62)	4.45 (5.29)	8.24 (8.71)	-
C <sub>1</sub> [PdL <sub>I</sub> Cl <sub>2</sub> ].05 H <sub>2</sub> O. 0.5 EtOH (yellow)	(287) decomp. 38%	-	-	-	20.75 (20.73)
C <sub>2</sub> [PtL <sub>I</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub> .2H <sub>2</sub> O.EtOH (yellow)	(259-261) sub. 43.8%	28.54 (28.67)	2.55 (2.52)	4.75 (3.72)	-
C <sub>3</sub> [RuL <sub>I</sub> Cl <sub>3</sub> H <sub>2</sub> O].2H <sub>2</sub> O (greenish black)	>(300) 25.4%	33.48 (34.29)	2.98 (3.57)	5.8 (5.0)	17.81 (18.05)
HL <sub>II</sub> C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> SO (yellow)	(145-147) 54%	65.5 (66.06)	4.20 (3.93)	10.43 (11.01)	-
C <sub>4</sub> Co(L <sub>II</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (reddish brown)	(282) decomp. 33%	55.85 (55.85)	3.40 (3.66)	8.39 (9.31)	-
C <sub>5</sub> [Ni(L <sub>II</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> 2EtOH (orange)	>(305) 30.8%	-	-	-	8.43 (8.47)
L <sub>III</sub>	(189-190)	65.73	4.20	10.62	

$C_{14}H_{10}N_2SO$ (yellow)	lit.185 <sup>(12)</sup> 33%	(66.06)	(3.93)	(11.01)	-
$C_6$ [PdL <sub>III</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O (Olive green)	>(305) decomp. 44.5%	-	-	-	19.33 (20.71)
$C_7$ [Pt(L <sub>III</sub> ) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub> .1.5H <sub>2</sub> O. EtOH(1) (pale yellow)	(259-260) decomp. 37.3%	37.45 (38.41)	2.58 (3.31)	5.82 (5.98)	19.76 (20.40)
$L_{IV}$ $C_{16}H_{15}N_3N_3S$ (orange)	(187-189) lit:(186-187) <sup>(13)</sup> 67.0%	59.34 (59.74)	4.92 (5.33)	14.50 (14.94)	-
$C_8$ [Co(L <sub>IV</sub> ) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].1.5H <sub>2</sub> O.EtOH (Grey violet)	(289-290) decomp. 20.9%	50.02 (50.92)	4.38 (5.36)	9.29 (10.48)	7.01 7.48
$C_9$ [Ni(L <sub>IV</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].(NO <sub>3</sub> ) <sub>2</sub> (orange yellow)	>(305) 29.3%	-	-	-	6.96 (7.46)
$C_{10}$ [Pd(L <sub>IV</sub> ) <sub>2</sub> Cl <sub>2</sub> ].3H <sub>2</sub> O.0.5EtOH (bright orange)	(259) decomp. (264-266) sub. 30.0%	-	-	-	13.31 (13.03)
$L_V$ $C_{12}H_{12}N_2SO_2$ (yellow)	(87-90) 20%	57.40 (57.99)	5.22 (4.83)	5.50 (5.64)	-
$C_{11}$ [Cu(L <sub>V</sub> )Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].0.2H <sub>2</sub> O (yellow)	(102-105) decomp. 15.8%	33.28 (32.69)	3.58 (4.17)	7.20 (6.36)	14.92 (14.43)

### c) Infrared spectra:

Important characteristic stretching frequencies of the ligands and their metal complexes are described in Table (3).

#### i) Complexes of L<sub>I</sub>(C<sub>1</sub>- C<sub>3</sub>) and L<sub>V</sub>(C<sub>11</sub>):

Bands related to methyl C-H, C-O, stretching and CH<sub>3</sub> bending vibrations of the ligand appeared at 2920, 1020 and 1355 cm<sup>-1</sup> respectively (17). All complexes C<sub>1</sub>-C<sub>3</sub> showed shifts in positions of azomethine group stretching vibrations, as a result of coordination with metal ions (9,22). The thiazole ring exhibited shifts of C=N, C-N and C-S stretching vibrations to higher frequencies in C<sub>1</sub> and C<sub>2</sub> and of C=N to lower frequencies in C<sub>3</sub>. This refers to the coordination of metal ion to sulfur atom (23) in C<sub>1</sub> and C<sub>2</sub> and to nitrogen atom (24) in C<sub>3</sub>. New low intensity bands were observed at lower frequencies were assigned to  $\nu_{M-S}$  and  $\nu_{M-N}$  vibrations respectively (25,26). Complexation of L<sub>IV</sub> with Cu(II) ion caused a shift of  $\nu_{C=N}$  of azomethine group only to higher frequencies which refers to the coordination of metal ion to imino nitrogen (9,22). A new low intensity band appeared at lower frequencies and was assigned to Cu-C<sub>1</sub> stretching modes of cis form (25).

#### ii) Complexes of HL<sub>II</sub> (C<sub>4</sub>, C<sub>5</sub>):

The spectra of C<sub>4</sub> and C<sub>5</sub> exhibited shifts in position of  $\nu_{C=N}$  vibrations and the disappearance of phenolic OH stretching modes together with the appearance of bands related to M-O and M-N=C stretching vibrations. This refers to the coordination of metal ions with imino nitrogen (9,22) and phenoxy group of the ligand (27, 28). Vibrations related to lattice water (25,26) were also observed.

#### iii) Complexes of L<sub>III</sub> (C<sub>6</sub>, C<sub>7</sub>):

The spectra of C<sub>6</sub> and C<sub>7</sub> showed shifts in stretching vibrations of azomethine group which refers to the coordination of azomethine group to metal ions (9,22). The spectrum of C<sub>6</sub> exhibited shifts of thiazole ring vibrations to higher frequencies which refers to further coordination of metal ion to sulfur atom (23).

Table (3): Characteristic stretching vibrations  $\nu(\text{cm}^{-1})$  of i.r spectra for Schiff bases and their metal complexes

Symbol	Thiazole vibrations			$\nu_{\text{OH}}$ Phenolic (EtOH)	$\nu_{\text{H}_2\text{O}}$ Lattice (coordinate)	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-Cl}}$	$\nu_{\text{M-S}}$ (NO <sub>3</sub> )
	Azome thine $\nu_{\text{C-N}}$	$\nu_{\text{C-N}}$	$\nu_{\text{C-S}}$						
L <sub>I</sub>	1610	1500	1105	730	-	-	-	-	-
C <sub>1</sub>	1595	1520	1120	750	3380-3270	420 <sup>a</sup>	-	335	375
C <sub>2</sub>	1630	1520	1130	750	3260-3200 (695pr), (645pw)	480 <sup>a</sup>	(390) <sup>g</sup>	335	420
C <sub>3</sub>	1585	1449	1120	745	3500-3200 (600)	420 <sup>a</sup> 260 <sup>b</sup>	(490) <sup>g</sup>	370 355 310	-
HL-II	1595	1500	1110	745	-	-	-	-	-
C <sub>4</sub>	1630-1595	1510	1110	745	(840 pr) (575 pw)	495 <sup>a</sup>	(460) <sup>d</sup> (405) <sup>g</sup>	-	-
C <sub>5</sub>	1630-1600	1513	1115	745	(700 pr) (690 pw)	500 <sup>a</sup>	(410) <sup>d</sup> (400) <sup>g</sup>	-	-
L-III	1621	1525	1105	745	-	-	-	-	-

Table (3): (continued)

Symbol	Azome thime $\nu_{C=N}$	Thiazole vibrations			$\nu_{OH}$ Phenolic (EtOH)	$\nu_{H_2O}$ Lattice (coordinate)	$\nu_{M-N}$	$\nu_{M-O}$	$\nu_{M-Cl}$	$\nu_{M-S}$ ( $\nu_{NO_2}$ )
		$\nu_{C=N}$	$\nu_{C-N}$	$\nu_{C-S}$						
C <sub>6</sub>	1610	1540	1130	754	(3600-3440)	3400-3290	440 <sup>a</sup>	-	350,320	410
G <sub>7</sub>	1630	1515	1110	745	(3700-3400) 3340	3206-3210 770pr 660pw	490 <sup>a</sup>	(415) <sup>b</sup>	320	-
L <sub>9v</sub>	1621	1525	1118	740	-	-	-	-	-	-
C <sub>8</sub>	1600	1520	1118	740	(3700-3500)	3480-3160 (660)	505 <sup>a</sup>	(435) <sup>b</sup>	300 295	-
C <sub>9</sub>	1600	1520	1118	740	-	(710) (660)	570 <sup>a</sup>	(490) <sup>b</sup>	-	(1400) (1280) (1018)
C <sub>10</sub>	1595	1520	1118	740	3600-3500	3380-3270	550 <sup>a</sup>	-	410,360	-
L <sub>v</sub>	1583	1500	1100	740	-	-	-	-	-	-
C <sub>11</sub>	1610	1510	1110	740	-	3630-3230 830pr,640pw	560 <sup>a</sup>	(470) <sup>b</sup>	380 330	-

(a)  $\nu_{M-N}$  of Schiff base, (b)  $\nu_{M-N}$  of thiazole ring; (c)  $\nu_{M-N}$  of Et<sub>3</sub>N (d)  $\nu_{M-N}$  of ligand; (e)  $\nu_{M-O}$  of M-OH; (f)  $\delta_{M-O}$ ; (g)  $\nu_{M-O}$  of H<sub>2</sub>O Hb= hydrogen bonded; sh= shoulder; pr= rockings; pw= wagging

**iv) Complexes of L<sub>IV</sub> (C<sub>8</sub> - C<sub>10</sub>):**

All complexes exhibited shifts in positions of azomethine group stretching vibrations only which indicates the coordination of nitrogen of this group to metal ions (9,22).

**d) Electronic spectra, magnetic susceptibility and conductivity measurements:****i) Electronic spectra of ligands:**

Table (4) describes the electronic spectra of the prepared Schiff bases in both DMF and ethanol. Two main bands were observed in the u.v region. The first band was assigned to  $\pi \rightarrow \pi^*$  transition

of the aromatic rings. The second band appeared at lower wavenumber was assigned to extended  $\pi \rightarrow \pi^*$  of the conjugated Schiff bases (17,19). It was difficult to locate bands assigned to  $n \rightarrow \pi^*$  transitions as they might be masked by  $\pi \rightarrow \pi^*$  bands. Complexation with metal ion caused shifts of ligand bands to lower wavenumbers and the appearance of new bands in the visible, and near i.r region. These additional bands may be related to M-L charge transfer bands and ligand field transitions.

Table (4): bands of maximum absorptions ( $\text{cm}^{-1}$ ) in electronic spectra of Schiff bases (L<sub>I</sub>-L<sub>V</sub>) with molar extinction coefficients  $\epsilon_{\text{max}}$  ( $1.\text{mol}^{-1}.\text{cm}^{-1}$ ).

Symbol	DMF		Ethanol	
	$\nu_{\text{max}} (\text{cm}^{-1})$	$\epsilon_{\text{max}} (1.\text{mol}^{-1}.\text{cm}^{-1})$	$\nu_{\text{max}} (\text{cm}^{-1})$	$\epsilon_{\text{max}} (1.\text{mol}^{-1}.\text{cm}^{-1})$
L <sub>I</sub>	31628	12341.00	25510	18555.50
	33278	13523.70	29046	19113.15
	36269	12212.50	33816	9183.31
HL <sub>II</sub>	31546	17326.80	43860	11629.79
	33333	16884.30	26022	6515.70
	36269	15389.10	31546	16746.90
L <sub>III</sub>	33333	14831.90	39526	18303.00
	36101	15648.30	21053	3303.60
			29851	8446.00
L <sub>IV</sub>	30395	34451.00	39063	18196.60
	36630	14400.00	23474	32778.34
			31348	4671.15
L <sub>V</sub>	26810	26754.90	36364	4765.60
	28571	32036.40	26525	27864.20
	34130	15215.20	28571	38741.70
	36969	12019.90	33010	12251.70
		41152	25745.00	
		45638	11589.00	

Table (5): describes bands of maximum absorption of complexes in DMF with their assignments together with crystal field parameters ( $10Dq$ ,  $B'$ ,  $10Dq/B'$  and  $\beta$ ). The letters were determined by applying band ratios

on Tanabe Sangano diagrams of the specified metal ion (30-33). All Complexes showed spectral behaviours related to octahedral geometries except Pd (II) complex

Table (5): Electronic Spectral data electrical conductivities (DMF  $10^{-3}$ ) Magnetic susceptibilities ( $\mu_{\text{eff}}$ , B.M) and suggested geometries for metal complexes of  $H_2L_1$  and Mixed ligands complexes.

A	Max. absorption $\nu_{\text{max}}(\text{cm}^{-1})$	Band assignment	Dq/B'	B' ( $\text{cm}^{-1}$ )	$\beta$	10Dq ( $\text{cm}^{-1}$ )	Conductivity $\text{Scm}^2\text{mol}^{-1}$	$\mu_{\text{eff}}$ BM	Suggested geometry
C1	$\nu_1$ 16393	$^1A_{1g} \rightarrow ^1A_{2g}$	-	-	-	20833	18.5	Diamag.	Square Planar
Pd(II)	$\nu_2$ 20833	$^1A_{1g} \rightarrow ^1B_{1g}$							
	$\nu_3$ 25906	$^1A_{1g} \rightarrow ^1E_g$							
C2	$\nu_1$ 21413	$^1A_{1g} \rightarrow ^3T_{1g}$ , $^1A_{1g}$					168.9	Diamag.	Square Planar
Pt(III)	$\nu_2$ 26881	$\rightarrow ^1T_{1g}$							
C3	$\nu_1$ 10537	$^2T_{2g} \rightarrow ^4T_{1g}(G)$					12.2	1.36	Octahedral
Ru(III)	$\nu_2$ 11628	$^2T_{2g} \rightarrow ^4T_{1g}(G)$							
	$\nu_3$ 21905	$^2T_{2g} \rightarrow ^2A_{2g}$ , $^2E_g$							
	$\nu_4$ 27778	CT(M $\rightarrow$ L)							
	$\nu_1$ 5974(calc-)	$^4T_{1g} \rightarrow ^4T_{2g}$	0.88	693	0.71	6099	9.8	5.7	Octahedral
Co(III)	$\nu_2$ 12392	$^4T_{1g} \rightarrow ^4A_{2g}$							
	$\nu_3$ 15385	$^4T_{1g}(F) \rightarrow ^4T_{1g}(p)$							
	$\nu_4$ 25641	CT(M $\rightarrow$ L)							
	$\nu_1$ 10537	$^3A_{1g} \rightarrow ^3T_{2g}$	1.9	527	0.51	10010	3.1	4.02	Octahedral
Ni(III)	$\nu_2$ 15700	$^3A_{2g} \rightarrow ^3T_{1g}(f)$							
	$\nu_3$ 23816(calc-)	$^3A_{2g} \rightarrow ^3T_{1g}(p)$							
	$\nu_4$ 21505	CT							
	$\nu_5$ 2641	$\pi \rightarrow \pi^*$							



Table (5): (continued)

Symbol	Max. absorption $\nu_{max}(\text{cm}^{-1})$	Band assignment	Dq/B'	B' ( $\text{cm}^{-1}$ )	$\beta$	10Dq ( $\text{cm}^{-1}$ )	Conductivity $\text{Scm}^2\text{mol}^{-1}$	$\mu_{\text{eff}}$ BM	Suggested geometry
C <sub>6</sub>	$\nu_1$ 20202 $\nu_2$ 25906	$^1A_{1g} \rightarrow ^1A_{2g}$ $^1A_{1g} \rightarrow ^1B_{1g}$	-	-	-	25906	4.7	Diamag.	Square planar
C <sub>7</sub>	$\nu_1$ 22222 $\nu_2$ 27397	$^1A_{1g} \rightarrow ^3T_{1g}$ $^1A_{1g} \rightarrow ^1T_{1g}$	-	-	-	-	116	Diamag.	Octahedral
C <sub>8</sub>	$\nu_1$ 6073 (cal.) $\nu_2$ 129532 $\nu_3$ 16547	$^4T_{1g} \rightarrow ^4T_{2g}$ $^4T_{1g} \rightarrow ^4A_{2g}$ $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$	0.88	752	0.77	6619	34.4	4.79	Octahedral
Co <sup>(III)</sup>	$\nu_4$ 23810	CT(M→L)	-	-	-	-	-	-	-
C <sub>9</sub>	$\nu_1$ 9320 $\nu_2$ 14661	$^3A_{2g} \rightarrow ^3T_{2g}$ $^3A_{2g} \rightarrow ^3T_{1g}(F)$	-	-	-	-	-	-	-
Ni <sup>(III)</sup>	$\nu_3$ 23319 (calc.) $\nu_4$ 23981	$^3A_{2g} \rightarrow ^3T_{1g}(P)$ CT	1.37	669	0.65	9172	156.6	3.7	Octahedral
C <sub>10</sub>	$\nu_1$ 16666 $\nu_2$ 20721 $\nu_3$ 23981	$^1A_{1g} \rightarrow ^1A_{2g}$ $^1A_{1g} \rightarrow ^1B_{1g}$ $^1A_{1g} \rightarrow ^1E_g$	-	-	-	24468	20	Diamag.	Square planar
Cu <sup>(II)</sup>	$\nu_1$ 12360 $\nu_2$ 16393	$^2B_{1g} \rightarrow ^2A_{1g}$ $^2B_{1g} \rightarrow ^2B_{2g}$	-	-	-	-	10.5	2.03	Octahedral

which showed square planer behaviours (30,31). The Cu(II) complex exhibited behaviours related to Jahn-Teller distortion of  $^2D$  term of octahedral complexes (31,34). The bands observed in Ru(III) complex are referred mainly to  $L \rightarrow M$  charge transfer and lie mainly near intraligand  $\pi \rightarrow \pi^*$  transition bands (30). Conductivity measurements of  $C_1$ ,  $C_3$ ,  $C_6$ ,  $C_8$ ,  $C_{10}$  and  $C_{11}$  in DMF ( $10^{-3}M$ ) showed that they were non electrolytes while  $C_2$ ,  $C_7$  and  $C_9$  were found to be electrolytic with ionic ratio of 1:2.

According to these observations and those obtained from CHN, A. A and thermal analyses and i.r spectra the structures of complexes were suggested as illustrated in Scheme -2.

#### e) Thermal analyses:

Thermal decomposition of some complexes by TG and DTG techniques are described in table (6) and thermographs for other complexes are shown in Figure (1). Results were in agreement with those obtained from CHN analysis and atomic absorption. Fragments which are not directly bonded to metal ion were found to leave at lower temperature than those directly bonded.

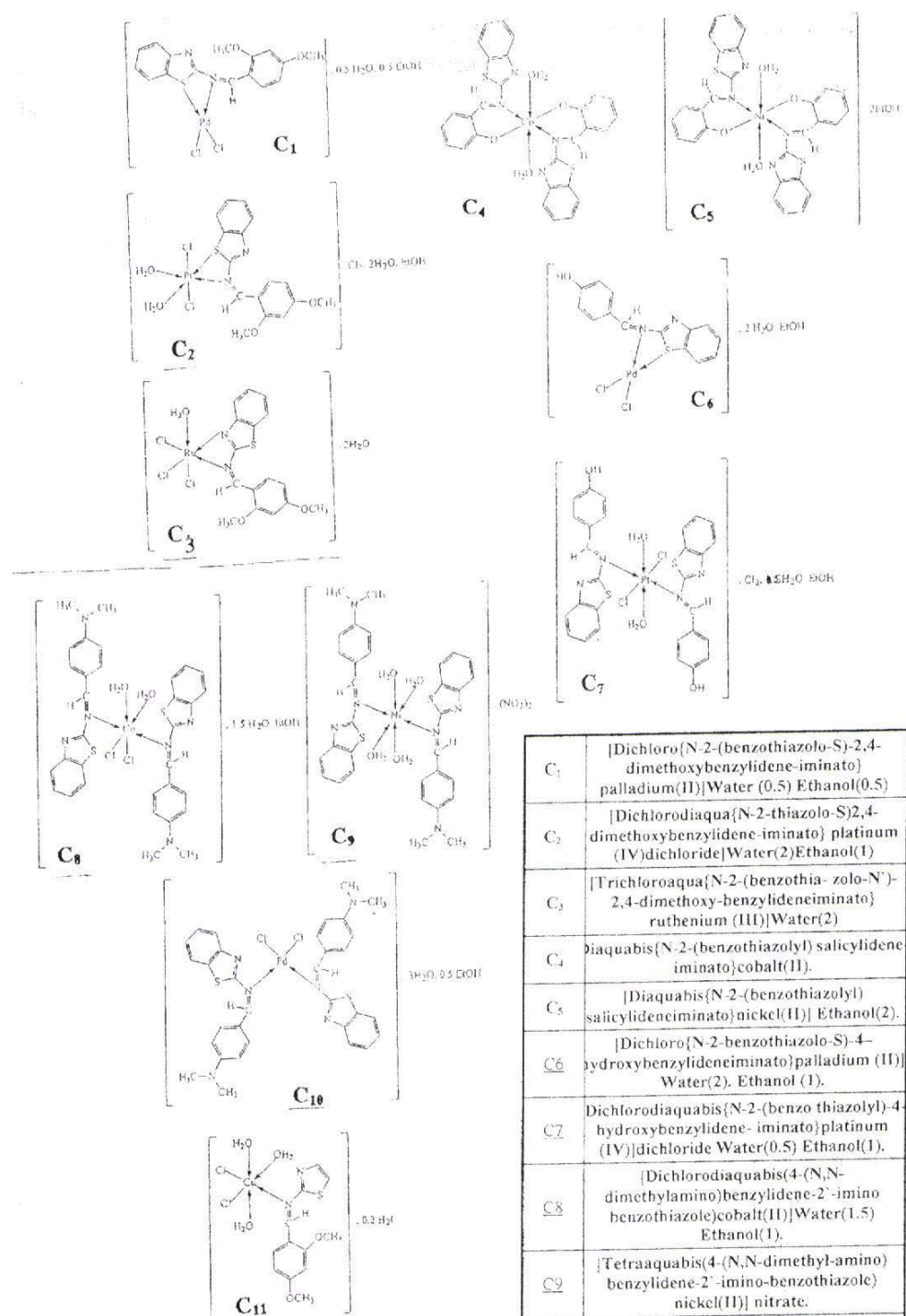
$C_1$  and  $C_6$  gave PdS as final product. This reflects the high affinity of Pd (II), ion to sulphide as both ions are soft acid and base respectively (35, 36). Different behavior was shown by  $C_9$  and  $C_{10}$  within the same temperature range of decomposition which reflects the higher affinity of Ni (II) ions towards nitrogen compared with Pd (II) ions (37).

#### f) Biological activity:

A preliminary study of biological activity of the prepared complexes was carried out in DMF (1 mg/ml) on two types of bacteria namely gram (-) E. Coli and gram (+) B. Subtuluse. The following results were observed.

No antibacterial actions were exhibited by the ligands except  $HL_{II}$  which showed growth inhibition diameter of 8-10 mm against E. Coli.

In contrast to their ligands complexes of Cu(II), Pd(II), Pt(IV) and Ru(III) showed successful variable antibacterial activity against both types.  $C_6$  and  $C_2$  showed growth inhibition of 10 and 8-10 mm diameter respectively against B. Subtuluse.



C <sub>1</sub>	[Dichloro(N-2-(benzothiazolo-S)-2,4-dimethoxybenzylidene-iminato) palladium(II)]Water (0.5) Ethanol(0.5)
C <sub>2</sub>	[Dichlorodiaqua(N-2-thiazolo-S)2,4-dimethoxybenzylidene-iminato} platinum (IV)dichloride]Water(2)Ethanol(1)
C <sub>3</sub>	[Trichloroqua(N-2-(benzothiazolo-N')-2,4-dimethoxy-benzylideneiminato} ruthenium (III)]Water(2)
C <sub>4</sub>	[Diaquabis(N-2-(benzothiazolyl) salicylidene iminato)cobalt(II).
C <sub>5</sub>	[Diaquabis(N-2-(benzothiazolyl) salicylidenciminato)nickel(II)] Ethanol(2).
C <sub>6</sub>	[Dichloro(N-2-benzothiazolo-S)-4-hydroxybenzylideneiminato]palladium (II)] Water(2). Ethanol (1).
C <sub>7</sub>	[Dichlorodiaquabis(N-2-(benzothiazolyl)-4-hydroxybenzylidene- iminato)platinum (IV)]dichloride Water(0.5) Ethanol(1).
C <sub>8</sub>	[Dichlorodiaquabis(4-(N,N-dimethylamino)benzylidene-2'-imino benzothiazole)cobalt(II)]Water(1.5) Ethanol(1).
C <sub>9</sub>	[Tetraaquabis(4-(N,N-dimethyl-amino) benzylidene-2'-imino-benzothiazole) nickel(II)] nitrate.
C <sub>10</sub>	[Dichlorobis(4-(N,N-dimethyl-amino) benzylidene-2'-imino-benzothiazole) palladium(II)]Water(3) Ethanol(0.5).
C <sub>11</sub>	[Dichlorotetraqua(2,4-dimethoxy-benzylidene-2'-iminobenzothiazole)

Acheme (2): Suggested stereochemical structures and names of schiff base complexes

Table (6): Stages of thermal decomposition of Schiff base complexes  $C_1, C_2, C_6, C_9$  and  $C_{10}$ .

Stable phase $C_1$	Temp. range of decomposition at TG ( $^{\circ}C$ )	Peak Temp. at DTG ( $^{\circ}C$ )	Weight loss% found (Calc.)
$[PdL_1Cl_2] \cdot 0.5 H_2O \cdot 0.5 EtOH$			
↓-0.5 $H_2O$	(65-95)	65	3.31 (4.15)
↓-2( $OCH_3$ ) ↓- Cl	(95-260)	*	1.969 (1.76)
↓-Ph ↓- PhCHN	(335-420)	410	35.43 (34.71)
↓-CN	(420-480)	445	5.51 (5.07)
PdS			27.95 (27.01)
$C_2$			
$[PtL_1Cl_2(H_2O)_2] \cdot Cl_2 \cdot 2H_2O \cdot EtOH$			
↓-EtOH	(65-150)	*	5.81 (6.11)
↓-2 $H_2O$ ↓- 2Cl	(150-230)	225	14.12 (14.20)
↓-2 $H_2O$ ↓- Ph	(230-300)	270	14.93 (14.86)
↓-( $OCH_3$ ) <sub>2</sub> PhCHN	(300-410)	*	21.16 (21.77)
$Cl_2Pt \leftarrow SCN$	(410-500)	445	17.01 (17.31)
$C_6$			
$[PdL_{III}Cl_2] \cdot 2H_2O \cdot EtOH$			
↓-2 $H_2O$ ↓- EtOH ↓- Cl	(101-375)	349	22.59 (22.87)
↓-Ph ↓- CHN	(387-428)	393	20.03 (20-05)
↓-PhOH	(428-590)	489	19.39 (18.10)

Table (2): Continued

Stable phase C <sub>6</sub>	Temp. range of decomposition at TG (°C)	Peak Temp. at DTG (°C)	Weight loss% found (Calc.)
↓-CN ↓-Cl	(796-825)	812	11.38 (11.97)
↓PdS	(825-1000)	*	25.16 (26.96)
C <sub>9</sub>			
[Ni L <sub>IV</sub> (H <sub>2</sub> O) <sub>4</sub> ] .(NO <sub>3</sub> ) <sub>2</sub>			
↓- 2NO <sub>3</sub>	(25-220)	205	15.32 (15.75)
↓-4H <sub>2</sub> O	(220-300)	275	9.27 (9.15)
↓-N(CH <sub>3</sub> ) <sub>2</sub> Ph CHN ↓- 2Ph	(300-405)	370	37.09 (37.98)
↓-2NCS	(405-438)	410	14.11 (14.76)
N(CH <sub>3</sub> ) <sub>2</sub> PhCHN→Ni			25.0 (26.13)
C <sub>10</sub>			
[PdL <sub>IV</sub> ]Cl <sub>2</sub> .3H <sub>2</sub> O.0.5 EtOH			
↓-0.5 EtOH	(35-125)	65	2.40 (2.82)
↓-H <sub>2</sub> O	(125-165)	150	2.05 (2.20)
↓-H <sub>2</sub> O	(125-165)	150	2.05 (2.20)
↓-2H <sub>2</sub> O	(165-205)	*	4.50 (4.41)
↓-2Ph	(205-300)	*	19.66 (18.61)
↓-2N(CH <sub>3</sub> ) <sub>2</sub> Ph CHN	(300-405)	325	34.81 (35.99)
PdCl <sub>2</sub> + 2NCS			34.81 35.99

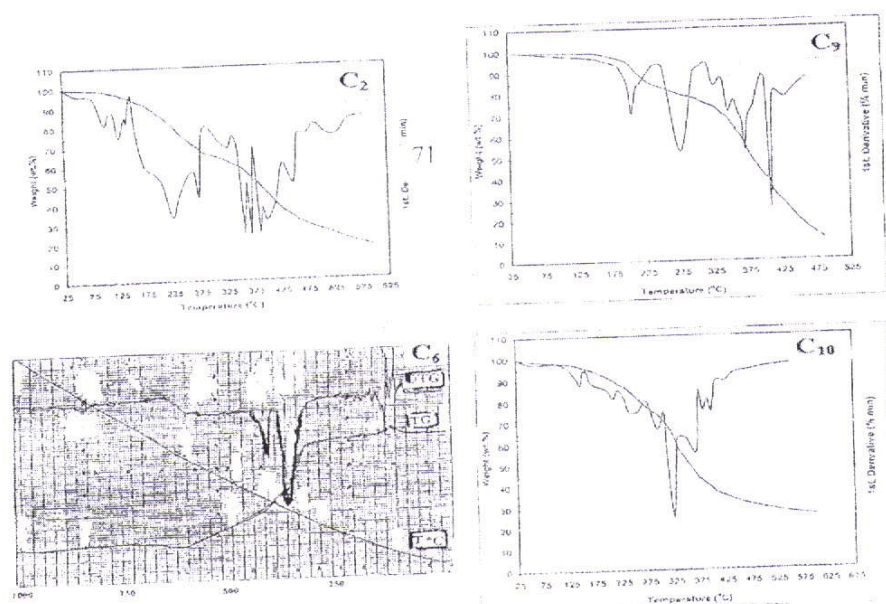


Figure (1): Thermograms of TG and DTG showing thermal behaviours of C<sub>2</sub>, C<sub>6</sub>, C<sub>9</sub> and C<sub>10</sub>

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