Synthetic & Analytic Study of Complexes of Some Transition Elements with 5-Phyenyl Amino-3-Salicylidimino- 1,2,4 Thiadizole

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Abstract

The new Schiff base 5-phyenyl amino-3-Salicylidimino- 1,2,4 thiadizole (HL) was prepared from condensation reaction of 3-amino-5-phenyl amino-1,2,4-thiadiazole with salicyldehyde. Complexes with some selected metal ions Cr(III) ,Fe(III), Zr(IV), pd(II) and pt(IV) were prepared by reacting the ligand with the hydrated metal chlorids $CrCl_3.6H_2O$, $FeCl_3.6H_2O$, $ZrOCl_28H_2O$, $PdCl_2$ ...and K_2PtCl_4. $2H_2O$ in the presence of 5% triethyl amine solution Et_3N. The elemental analysis (C.H.N.M), electronic spectra (Uv-Vis spectra) showed that molar ratio of metal : ligand was 1:2. The F.T.I.R. spectra , Molar conductivity (Λm) and magnetic susceptibility of complexes were also determined .

Introduction:

Many metal complexes of Schiff bases have been used as synthetic models of biological molecules and as catalysts in chemical industries(1,2) . The presence of azomethine group with alone pair of electrons on the nitrogen atom provides abinding site for coordination between schiff bases and ametal ion(3).Interests have been concentrated on schiff bases having two or more donor atoms(4-11) .Some of these complexes were suggested as models for enzyme activity such as galactose oxidase(12).

In the present work we report synthesis of the new Schiff base , 5-phyenyl amino-3-Salicylidimino- 1,2,4 thiadizole and some metal complexes.

Experiment:

Melting points were recorded on a Gallen Kamp M.F.B 600F melting point apparatus .U.V-Visible spectra were recorded on Shimadzu U.V-Vis. 160 spectrophotometer in the range (200-1000)nm using absolute ethanol and dimethyl formamide (DMF) as solvents . Infrared spectra were recorded on F.T.I.R 8300 shimadzu spectrophotometer , and all samples were prepared as KBr or CsI-discs.

Elemental microanalysis was carried out using C.H.N. elemental analyzer model perkin-Elmer B-240.

Conductivity measurements were made on 10^{-3} M solution of the complexes at 25C° using a PW 9526 digital conductivity meter.

Magnetic measurements were carried out by using Magnetic susceptibility Balance Johnson mattey catalytic system division via Gouys method.

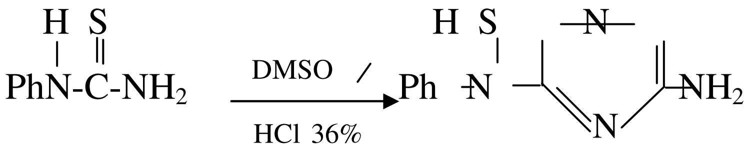
All chemicals used were of reagent grade(B.D.H and Fluka) and used as supplied .

3-amino-5-phenylamino-1,2,4-thiadiazole (TZ) was prepared according to literature method(13) (scheme 1).

1. Preparation of the Schiff base (HL):

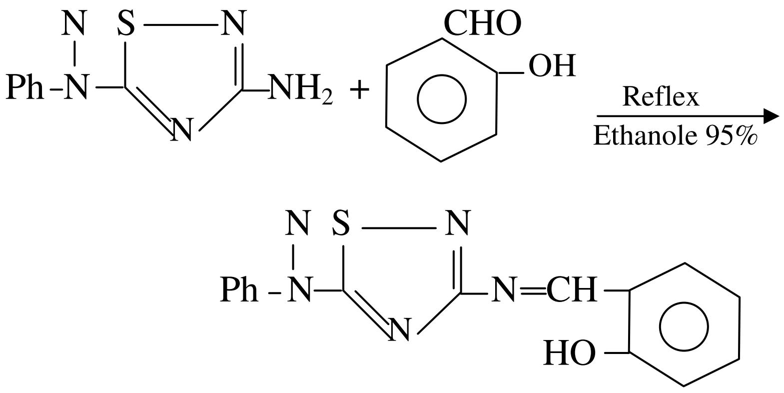
An-ethanolic solution of 3-amino-5-phenylamino-1,2,4-thiadiazole (TZ) (0.01 mole , 1.92 gm) was added to a solution of (0.01 mole , 1.22 gm) 2-hydroxy benzaldehyde (Salicyldehyde) dissolved in 20ml of 95% ethanol.

The mixture was refluxed gently for 1.5 hours , upon cooling , a yellow solid mass was separated .the product was recrystallized from ethanol , to afford bright yellow crystals of (HL) (2.22 gm , 75% yield).



(TZ)

Scheme(1)



(HL)

Scheme(2)

2. Preparation of the metal complexes:

a) preparation of metal complexes (C_1 , C_2 and C_3):

An.ethanolic solution of (0.01 mole) of each of the following metal chlorides ($CrCl_3.6H_2O$, $FeCl_3.6H_2O$ and $ZrOCl_2.8H_2O$)in 5 ml of triethyl amine was added to an-ethanolic solution of (0.02 mole) of the ligand (HL) .

The mixture was heated under reflux for (30-45) minutes , the solvent was removed under vaccum evaporization , cooled , aprecipitate was formed and the product(50-70%) was recrystallized from ($DMF:H_2O$) and dried under vaccum(Table 1)

b) preparation of C_4 and C_5 complexes:

An-ehtanolic solution of (0.01 mole) of $Na_2[PdCl_4]$ or $K_2[PtCl_6]$ was added to an ethanolic solution of (0.02 mole) of (HL) ligand with stirring . Precipitates were found immediately, stirring was continued for an-hour to ensure completion of reaction .The products were filtered off ,washed with hot ethanol , followed by cold water , and then dried under vaccum .Recrystallization from ($DMF:H_2O$) afforded bright crystals of 80-90% yield.Table(1).

Table (1) Physical properties of the ligand (HL) and its metal complexes

No.	Symbol	Formula	Colour	M.P.C$^{\circ}$	%yield	Λ m^a (ohm^{-1}cm^2/mol)	K$_f$ Mol/lit^2	$\mu_{ef.}$ B.M
1	HL	$C_{15}H_{12}N_4SO$	Pale orange	215-217	75			
2	C_1	$[Cr(L)_2Cl]Cl$	Dark green	260-262	55	45	2.7×10^5	3.25
3	C_2	$[Fe_2L_2Cl_4].2H_2O$	Pale brown	273^d	60	25	1.6×10^6	5.6
4	C_3	$[ZroL_2].2H_2O$	Pale yellow	278-280	58	18	3.9×10^4	-
5	C_4	$[PdL_2]$	Deep orange	265-267	85	15	2.9×10^5	-
6	C_5	$[PtL_2Cl_2]$	Greenish yellow	290^d	90	25	6.9×10^6	-

Where : a = molar conductivity in dimethl formamide solvent(10^{-3}M) .

B = Formation constants in solution .

and d = decomposition .

Table (2) C.H.N.M elemental analysis for the prepared complexes

Compounds	Calc. (found)			
	C%	H%	N%	M%
HL	60.81 (60.01)	4.05 (3.91)	18.91 (19.10)	
C_1	40.39 (49.95)	3.08 (2.69)	15.73 (16.21)	7.28 (6.82)
C_2	32.74 (32.00)	3.18 (2.75)	12.74 (13.11)	12.69 (12.51)
C_3	39.27 (38.81)	3.54 (3.01)	15.27 (15.81)	12.41 (11.87)
C_4	41.35 (39.52)	3.16 (2.21)	16.09 (16.51)	15.28 (14.61)
C_5	33.64 (33.11)	2.57 (1.88)	13.08 (14.1)	22.78 (21.95)

3. Results & Discussion:

3-1 Physical and analytical data:

Table (1) describes the colors , melting points molar conductivity (Λm) in D.M.F solvent and the values of formation constants K_f in solution. The solids were stable toward air , moisture and light in solution.

Results from elemental analyses (table 2) of most complexes were found to be in agreement with the calculated values.

The molar ratio of metal ion to the ligand (M:L) was detected by Job-method(14) , and was found to be 1:2 ratio , morever the stability constants (K_f) values indicate the stability of the prepared complexes in solutions .

(figures 1 , 2).

Table (3): distinct vibrational frequencies (I.R ν cm^{-1}) and the electronic spectra (UV-Vis.) of the compounds

Compounds	I.R.(ν cm^{-1})	λ max (nm) , ε max mol^{-1}. $Lit.cm^{-1}$
HL	3500 (br.),1620 (s), 1350 (m) ,3180 (w)	215 (5700) ,320 (950)
C_1	1580(s),3120(m),500(w),410 ,250 (w),1365(s)	220,318(900),430 (80) ($A^4{}_{2g} \longrightarrow T^4{}_{2g}$),613 (80) ($A^4{}_{2g} \longrightarrow T^4{}_{1g}$)
C_2	3180(m),1570 (s),490 (w), 420,250-220 (w),1370 (s)	235,330 (1500),450,650 (120) ($A^6{}_{1g} \longrightarrow T^4{}_{1g}, E_g{}^4$)
C_3	3200(m),1560 (s),395, 815(s),1360 (s)	230,305(820),390 (20500) (L$\longrightarrow$ M Zr =O)
C_4	3100(m),1570 (s), 1370(s),425(m)	220,315(850),420(90) ($A^1{}_{1g} \longrightarrow B\ {}^1{}_{1g}$),370(150)($A_{1g} \longrightarrow E\ {}^1{}_{1g}$)
C_5	3180(m),1590 (s),1360 (m) ,410-300(w)	210,400 (80) ($A_{1g} \longrightarrow T^3{}_{2g}$)

3-2 Infra - Red Spectra:

Table (3), describes the important vibrations and assignments of the ligand and its metal complexes .The ligand exhibited abroad band at frequency region 3180-3500 cm^{-1} which was assigned to a phenolic OH overlapped with primary amino group of Ph-NH(15).the position of this band was shifted to 3100-3200cm^{-1} in the prepared complexes which indicates the deprotonation of phenolic –OH group in the basic medium (Et_3N) and participation of the oxygen atom or phenoxide moiety (phō-) in coordination with the metal ion (16).

Stretching mode of azomethine group (-CH=N) of the ligand appeared at 1620cm$^{-1(17)}$. The position was shifted to lower frequencies in metal complexes . Spectra which refers to the coordination of metal ions to nitrogen atom of azomethine group$^{(18)}$.

These observations were further indicated by the appearance of M-O , M-N and M-Cl bands at (425-500) , (395-410) and (200-300) cm$^{-1(19)}$.

3-3 Electronic Spectra:

The electronic spectra of the metal complexes were recorded for their solution in D.M.F. solvent in the range(200-900)nm.

C_1: This complex exhibited three absorption bands in the visible region at wave numbers 16313.2 , 23255.8 and 31446.5 cm^{-1} which were assigned to the transitions $A_2g^4 \longrightarrow T_1g^4$, $A_2g^4 \longrightarrow T_2g^4$ and $A_2g^4 \longrightarrow T_1g^4$ (P)$^{(20)}$ respectively of an octahedral chromium Cr (III) complex.

Magnetic moment (μ_{eff} =3.25 B.M) shows that the complex was paramagnetic which is characterized of high spin 3d^3 electronic configuration.

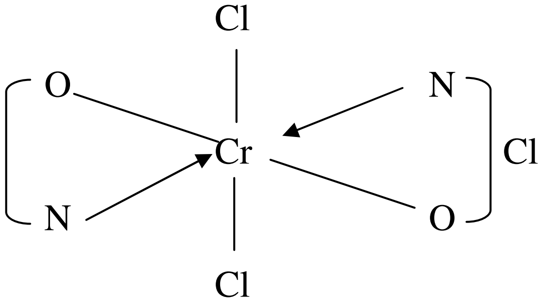
C_2: One broad absorption band appeared in the visible region at $\bar{\nu}$ = 22222.2 cm^{-1} and was assigned to the overlapped transitions of $A_{1g}^6 \longrightarrow T_{1g}^4$ and $A_{1g}^6 \longrightarrow E_g^{4\ (21)}$, which is in agreement with trigonal bipyramid complexes of Fe(III). The magnetic moment (μ_{eff} =5.6 B.M) indicates the ferromagnetic property of high spin 3d^5 configuration of Fe (III) complexes.

C_3: The electronic spectra of most Zr (IV) complexes are difficult to explain due to the formation of high intensity L ⟶ M charge transfer bands$^{(22)}$. One band was observed at ν =25641.02cm^{-1} and was assigned to the transition O ⟶ Zr of Zirconyl group.

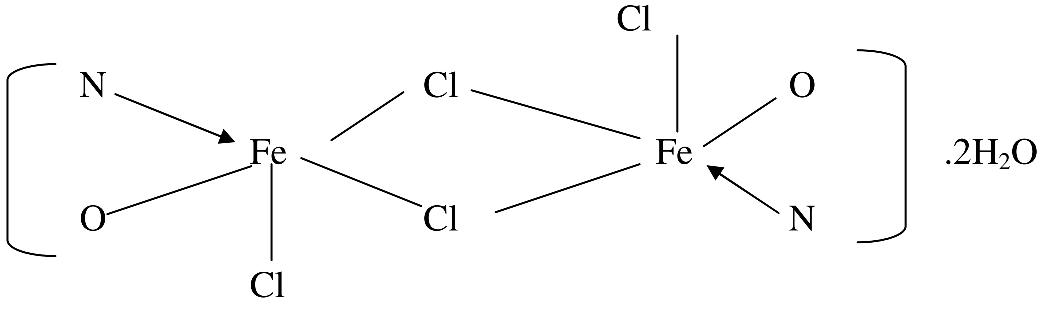
C_4: Two low intensity bands were observed in the visible region of this complex at $\overline{\nu}$ = 23809.52 and 27027.02cm^{-1} and were characteristic of Pd(II) square planar complex.

C_5: Only one low intensity band was observed at 25000cm^{-1} and was assigned to the transition $A_{1g}^{1} \longrightarrow T_{2g}^{1}$ of octahedral Pt(IV) complex(23).

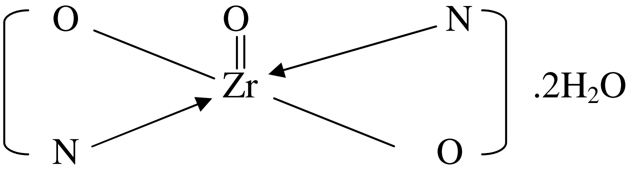
According to the above mentioned results from elemental and spectral data , as well as magnetic moments , the suggested structures of the prepared metal complexes may be illustrated as follows:



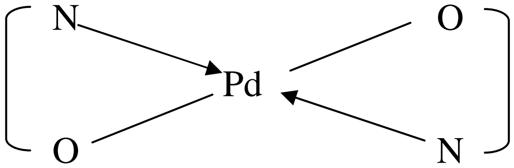
Bis [5-phenyl amino-3-Salicylidiminato- 1,2,4 thiadizole] dichlore Chromium (III) Chloride.



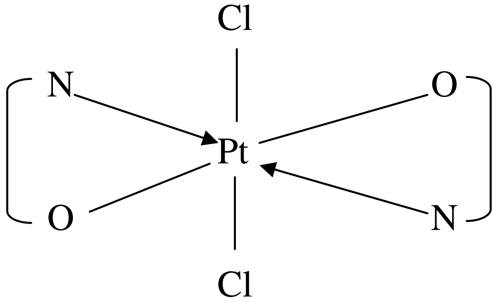
Di-μ-Chloro-bis[5-phyenyl amino-3-Salicylidimino- 1,2,4 thiadizole] chloro- Iron(III) Dihydrate.



Bis(5-phyenyl amino-3-Salicylidiminato- 1,2,4 thiadizole]oxo-Zirconium(IV). Dihydrate.

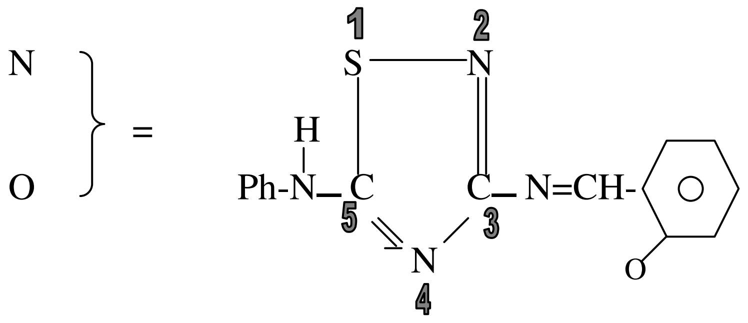


Bis[5-phyenyl amino-3-Salicylidiminato- 1,2,4 thiadizole] Paladium(II)



Dichloro-bis[5-phyenyl amino-3-Salicylidiminato- 1,2,4 hiadizole] Platinium(IV)

Where:



[5-phyenyl amino-3-Salicylidiminato- 1,2,4 thiadizole]

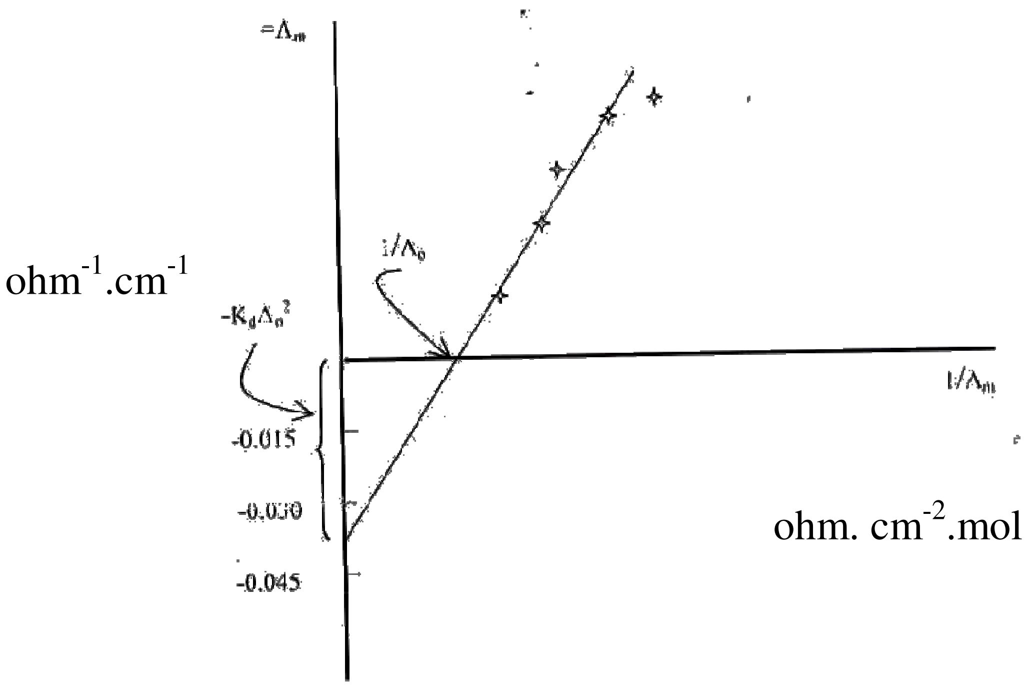


Fig. (1)calculation of K_d-constant [Pt_2 (DPYT)$Cl_4(H_2O)_4$]Cl

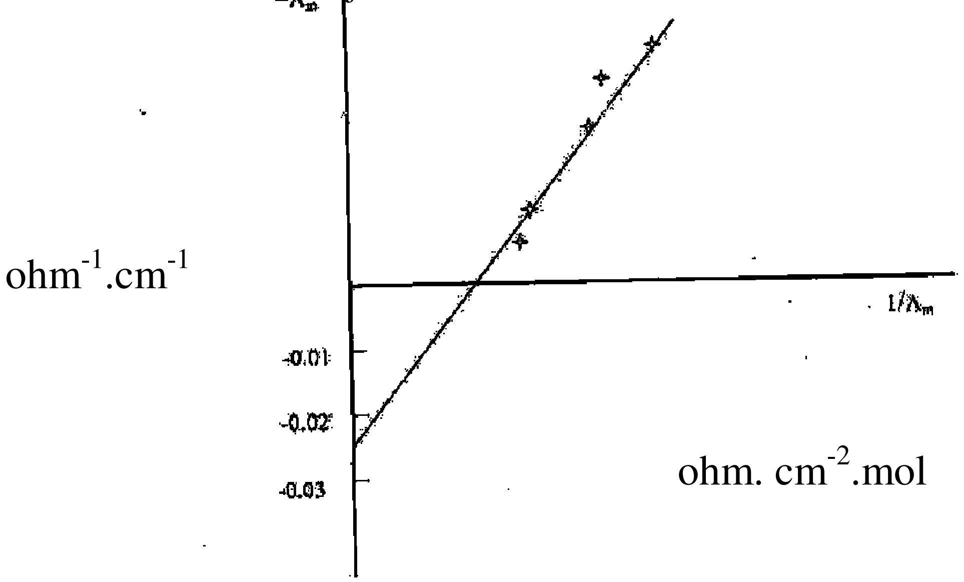


Fig. (2)calculation of K_d-constant [ZrO-ETD-complex]

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دراسة تحضيرية وتحليلية لبعض مركبات العناصر الانتقالية مع 5-فنيل أمينو -3- ساليسالديمينو-1 ، 2 ، 4 ثايادايازول

الخلاصة :

حضرت قاعدة شيف الجديدة 5- فنيل أمينو-3- ساليسالديمينو-1 ، 2 ، 4 ثايادايازول(HL) من تفاعل التكثيف بين 3- امينو-5 - فنيل أمينو-1 ، 2 ، 4 ثايادايازول والساليسالديهايد . وحضرت معقدات الليكاند (HL) مع بعض ايونات الفلزات المنتخبة ، وهي : الكروم الثلاثي ، والحديد الثلاثي ، وآيون الزركونيل ، والبلاديوم الثنائي ، والبلاتين الرباعي من تفاعل الليكاند مع كلوريدات الفلزات المذكورة المتميهة بوجود ثلاثي أثيل امين كقاعدة .

بينت نتائج التحليل الدقيق للعناصر (C.H.N.M) والدراسات الطيفية الالكترونية أن نسبة الفلز إلى الليكاند في جميع المعقدات المحضرة كانت 1 : 2 .

وأجريت أيضًا قياسات أطياف الأشعة تحت الحمراء المعززة بتحويلات فورير ، فضلاً عن قياسات التوصيل الكهربائية والحساسية المغناطيسية للمعقدات .