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Synthesis and Modification of Some New Transition Metal Complexes of Poly (vinyl chloride)

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Abstract:

Theligand4-[5-(2-hydoxy-phenyl)- [1,3,4- thiadiazole-2- ylimino methyl]-1,5-dimethyl -2-phenyl-1,2-dihydro-pyrazol-3-one [HL1] is prepared and characterized. It is reacted with poly(vinyl chloride) (PVC) in THF to form the PVC-L compounds ,PVC-L interacted with ions of transition metals to form PVC-L-M^{II} complexes .All prepared compounds are characterized by FTIR spectroscopy, u.v-visible spectroscopy, C.H.N.S. analysis and some of them by ^{1}HNMR .

Key words: PVC, Schiff Base, Heterocyclic Compounds, Modified Material, Inorganic Polymer

Introduction:

The coordination chemistry of nitrogen-sulfur donor chelating agents has mainly been studied with transition metals [1]. Newly there is a wide interest in these type especially with their metal complexes [2] because of their bioactivity [3]. Schiff bases are widely used in industry and have a range of biological activities. They are widely used organic compounds. They are used as dyes and pigments, intermediates, catalysts and polymer stabilizers [4]. Polymer-bound chelating ligands have a dynamic field of examination in polymer science. It gives a path to modify the polymer for the required application. Next to no data seems to exist with reference to whether such metal particle complexation can impact the characteristics of the macromolecule [5-7]. Newly, scientists are able to modify polymers [8-10]. PVC can compound with aromatic and heterocyclic bisection through the halogen compensation reaction. The chlorine displacement from poly(vinyl chloride) demonstrates the likelihood on easy anchoring of ligands to PVC matrix and the subsequent synthesis of immobilized transition metal complexes.

Material and Methods:

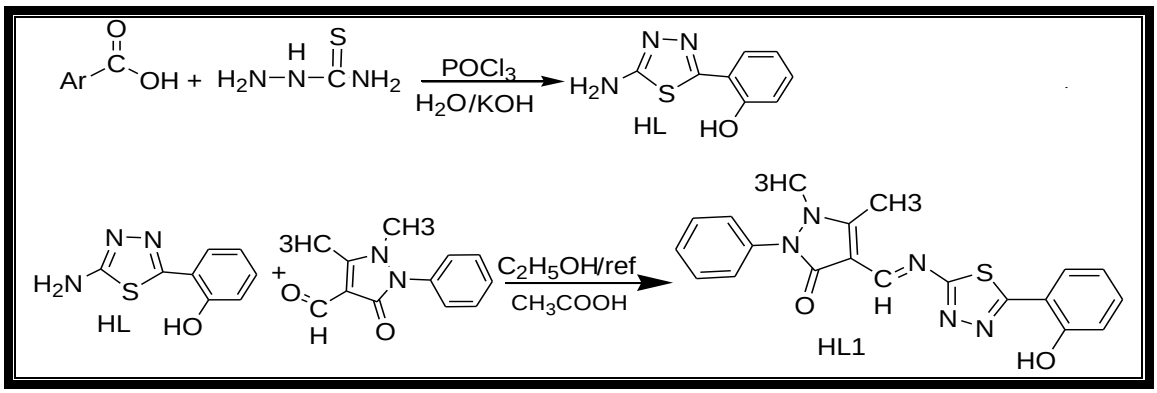
1- Synthesis of [2-amino-5-(2-hydroxy- phenyl-1,3,4-thiadiazole] [HL]

Salicylic acid (0.1 mol12.2g), thiosemicarbazide (0.1 mol 9.1 g) and (40ml) of $POCl_3$ are mixed and heated for 4 hours. After cooling (250 ml) of water is added and refluxed for (5)

hours. The mixture is cooled and filtered,the filtrate is neutralized with KOH conc. and recrystalized from ethanol. C.H.N.S analysis as shown on in Table (1).

2-4-[5-(2-hydoxy-phenyl)- [1,3,4-thiadiazol -2-ylimino methyl] -1,5-dimethyl- 2-phenyl-1, 2-dihydro-pyrazol-3-one [HL1]

Equimolar quantity (0.09 mol) of appropriate (4-antipyrincarboxaldehyde) and the (2-amino-5-(2-hydroxy-phenyl-1,3,4-thiadiazole), are mixed in free CH_3COH (15 ml) with two drops of G.A.A and refluxed for four hours. Then cooling the mixture at 25 C, the product was filtered. Ethanol was used for recrystallization to give an yellow powder. CHNS data given on Table (1).



Scheme (1) Synthesis of Ligand HL1

3- PVC Purification

Commercial PVC is purchased from Pet Kim Company (Turkey) re-precipitated from tetrahydrofuran solution in ethanol, then dehydrated under reduced pressure at 25 C for one day.

4-Preparation of PVC Ligand Compound

THF was used to dissolve PVC (0.1 mole) and (0.05 mol) was added from a prepared ligand then pyridine (few drops) was added. Then the mixture was refluxed for five hours. The precipitation achieved by separating the solvent using evaporator process.

5-Preparation of PVC Ligand Complex [11]

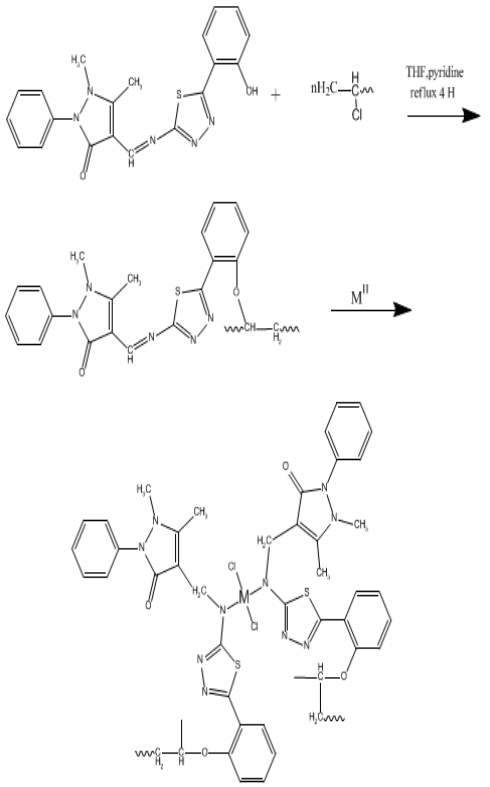
PVC-L-M^{II} complexes are carried out by reaction (0.5 mol) of the transition metal salt in CH_3COH and (1.5 mol) of PVC-L in 1,2 dichloromethane. The obtained colored precipitates and washed with excess of absolute CH_3COH. Scheme (2) presents the mechanisum of the synthesis of PVC-L-M^{II} polymer.

Table (1)The C.H.N.S Analysis Data of the Prepared Compounds

Compound Formula,	N	H	C	S
HL $C_8H_7N_3OS$	(21.75) 21.77	(3.65) 3.62	(49.73) 49.70	(16.59) 16.55
HL1 $C_{20}H_{17}N_5O_2S$	(61.37) 61.20	(4.38) 4.30	(17.89) 18.19	(8.19) 8.24

6-Films Preparation

In the preparation of the film, (5g/100ml)of PVC and PVC-L- M^{II} solution in THF was used to prepare different films of polymer. Evapouration technique was used to prepare the films at 25 C for one day and using micrometer sort 2610 A, Germany, for measuring.



Scheme (2) Synthesis of PVC-L- M^{II}

Results and Discussion:

Table (2) shows some physical data for the prepared compounds, while Table (3) shows electronic absorption bands for ligand, PVC-L and PVC-L-M^{II}. The bands that occurred are mainely categorious into 3 groups: the first appears in the ultra-violet region which refer to the intermolecular transitions; the other appears in the visible region which refers to d-d transitions, and the third is charge transfers from ligand to metal. These transitions are applicable to the Uv.vis spectrum of compounds.

Table (2) Some Physical Data for the Prepared Compounds

Symbol	Dec. Point ^{0}C	Color	Yield%
HL	236	White-pink	75%
HL1	281	Green	67%
Co(II)	283	Red blue	59%
Ni(II)	310	Pale green	73%
Cu(II)	318	Dark Green	79%

Table (3) Electronic Spectra for Ligand ,PVC-L and PVC-L-M^{II}

Symbol	Electronic absorption peaks (nm)	Assignment
HL	295	$\pi\rightarrow\pi^*$
	320	$n\rightarrow\pi^*$
HL1(L)	250	$\pi\rightarrow\pi^*$
	370	$n\rightarrow\pi^*$
PVC-L	250	$\pi\rightarrow\pi^*$
PVC-L-Co	225	$\pi\rightarrow\pi^*$
	243	$n\rightarrow\pi^*$
	320	Charge Transfer
	380	$^4T_1g^{(F)}\rightarrow{}^4t_1g^{(p)}$
	910	$^4T_1g\rightarrow{}^4A_2g$
PVC-L-Ni	235	$\pi\rightarrow\pi^*$
	295	$n\rightarrow\pi^*$
	320	Charge Transfer
	633	$^3A_2g\rightarrow{}^3t_1g^{(p)}$
	960	$^3A_2g\rightarrow{}^3t_1g^{(F)}$
PVC-L-Cu	230	$\pi\rightarrow\pi^*$
	295	$n\rightarrow\pi^*$
	360	Charge Transfer
	675	$^2Eg\rightarrow{}^2T_2g$
	595	$^4A_2g\rightarrow{}^4t_1g$
	655	$^4A_2g^{(F)}\rightarrow{}^4t_1g^{(p)}$

The Fourier transform infrared spectroscopy spectrum of compound (HL) Figure (1) shows two bands in the range (3396–3283) cm^{-1} which could refer to symmetric and asymmetric stretching vibrations of NH_2 group. Band in the (3101) stretching vibrations of (OH). At about (1626 cm^{-1}) ,there is a band due to cyclic (C = N) stretching, while the (N-H) bending and (C-N) stretching vibrations, occurs in (1518 cm^{-1}) and (1484 cm^{-1}) respectively [12].

The Fourier transform infrared spectroscopy spectra of (HL1) show the passing of the two IR bands of stretching of (-NH_2) thiadiazole, [HL] shows all the predictable bonds for olefinic (C-H), (C=C) aromatic, exocyclic and endocyclic imine group. Stretching vibrations in addition to out of plane bending of substituted aromatic ring. All the prepared compounds, have a band around (1213-1253) cm^{-1} which refers to (=N-N=C-) cyclic group , 3429

cm-1, due to (υ OH Stretching of alcohol), 1651cm-1 due to (υ C=N Stretching of amine), 1554 cm-1, 1498 cm-1 which refer to pyrazolone ring, 1432 cm^{-1}, 1267.27 cm-1 which indicates thiazole ring, 11421 cm-1 (υ C-O Stretching of alcohol). The Fourier transform infrared spectroscopy spectra of the ligands give a band at 3429 cm^{-1} which refers to υ O-H (weakly H-bonded) ,while this band passing in all the complexes of the metal meaning that the elemination of proton of hydroxyl group of benzene ring during the chelation. [13]

In PVC-L the spectrum shows a strong band at ν(622) cm^{-1} which may refer to the ν(C-Cl) band which differs from PVC without modification ν(641) cm^{-1}.In the FTIR spectra of complexes there is a shifting in C-O frequency from 1342 cm-1 (in ligand) to the higher frequency 1379 cm-1 (in complexes) [13], and band is broad in the (3285-3378) cm^{-1} region due to υ O-H of intracted water.

In the ligand, there is a band at 1651 cm-1 which may refer to υ C=N (azomethine), and the N atom of imine group is in coordination by showing to shift with downward (Δυ = 10-18 cm-1) in υC=N

All the Infrared data of compounds are listed on Table (4).

Table (4) Infrared Data of the Prepared Compounds (cm^{-1})

Symbol	ν(C=N)	ν(C=O)	ν(C-N=N-C)	ν(M-O)	ν (O-H) H_2O	ν (O-H)	ν(M-N)
HL1	1651(s)	1606	1219-1253	-	-	3429	-
PVC-L-Co	1662(s)	1521	1238-1311	425(s)	3292	-	476(s)
PVC-L-Ni	1661(s)	1593	1585	442(s)	3285	-	498(s)
PVC-L-Cu	1633(s)	1607	1240-1308	481(s)	3378	-	570(s)

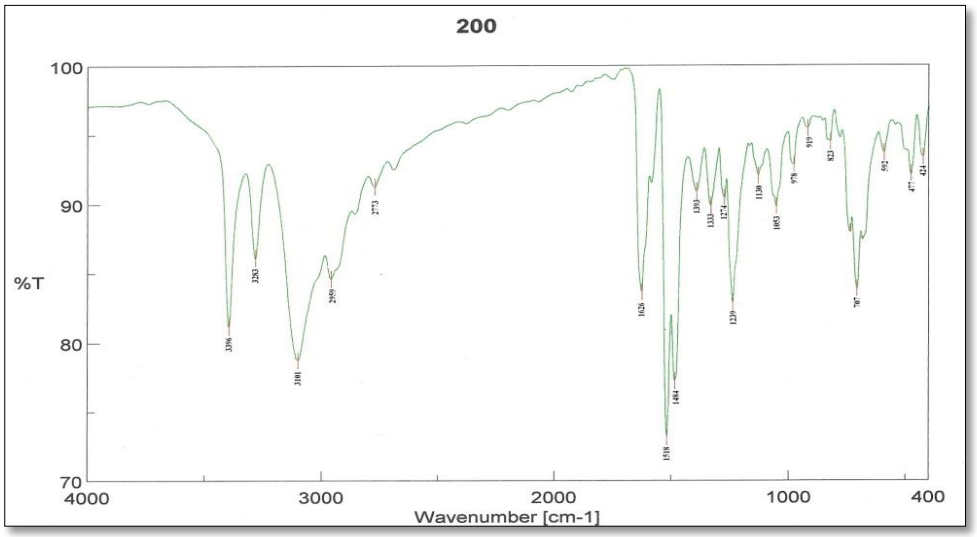


Fig. (1) Infrared Spectra of HL

^{1}H-NMR spectrum of compounds [HL1], Figure (2), shows the chemical shift, (CDCL3-d_6) ppm. The methyl protons resonate at [δ= 1.5, 2.4,3.4] (s, 3H, CH3), five aromatic ring protons of phenyl and four aromatic ring appear at (δ 6.9 – 7.6) ppm, proton C appears at (δ 7.8) Furthermore, the sign at (δ 8.8) assign to (C-H) proton, OH protonrosenate at ,(δ 11.7)

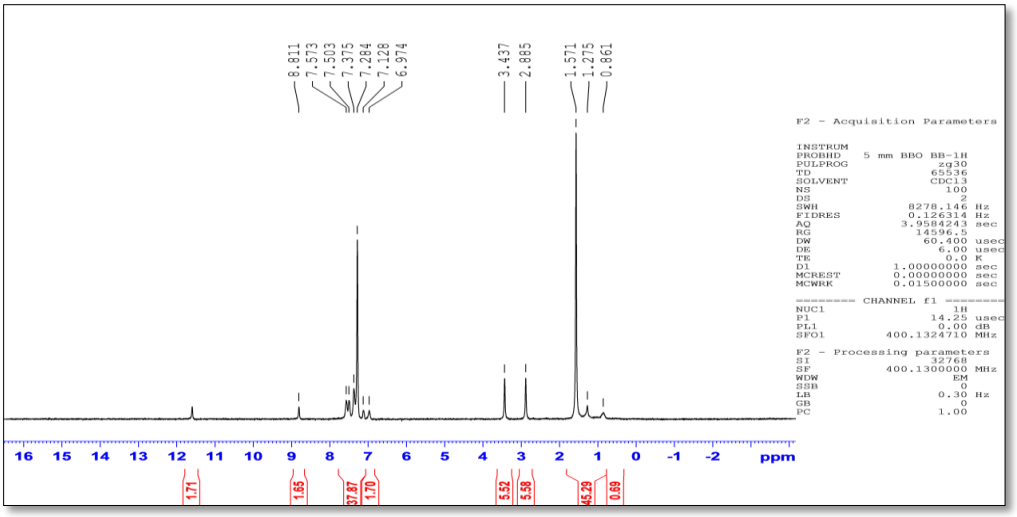


Fig. (2) ^{1}H-NMR Spectra of HL1

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تحضير وتعديل بعض معقدات العناصر الانتقالية لبولي فنيل كلورايد الجديدة

حنان عبد اللطيف ابراهيم

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الخلاصة:

تم تحضير المركب 4-[5-(2-هيدروكسي فنيل)- 4,3,1- ثايادايازول]-2-يل مثيل ايمين[5,1-ثنائي مثيل -2-فنيل-2,1- ثنائي هيدرو بايرازول -3-اون] وتم تشخيصه بتقنية الاطياف تحت الحمراء والاطياف الالكترونية والتحليل العنصري والطنين النووي المغناطيسي البروتوني .ثم تمت مفاعلة البولي فنيل كلورايد مع البيريدين كاربوهيدرازايد والذي تم مفاعلته مع عدد من العناصر الانتقالية لغرض تكوين المعقد $PVC\text{-}L\text{-}M^{II}$ تم تشخيص المعقدات بتقنية الاطياف تحت الحمراء والاطياف الالكترونية والتحليل العنصري

الكلمات المفتاحية :بولي فنيل كلورايد، اساس شيف، المركبات الحلقية غير المتجانسة، المواد المعدلة، البوليمرات اللاعضوية