

Synthesis and Characterization of some Mixed-Ligand Complexes Containing Salicylic Acid and Pyridine with some Metal Ions

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Abstract

Some metal ions (Mn^{+2} , Fe^{+2} , Co^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} and Hg^{+2}) Complexes of salicylic acid (SA) and Pyridine (Py) were Synthesized and characterized by elemental analysis FT-IR and uv-Visible Spectra and conductive measurements From the results obtained, the following general formula are given for the prepared complexes $[M^{+n}(SA)_2(Py)_2].XH_2O$, where $M^{+n} = Mn^{+2}, Fe^{+2}, Co^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}$, $n = 2$, $X = 0, 0, 6, 0, 5, 6, 6$; (SA^-) = ligand ion (Salicylato), (Py) = Pyridine

Keyword: Synthesis, complexes, pyridine and salicylic acid.

Introduction

Salicylic acid (SA) is a phenolic phytohormone and is found in plants with roles in plant growth and development [1]. Salicylic acid is biosynthesized from the amino acid phenylalanine and can be produced by sodium salicylate [2, 3]. In modern medicine, salicylic acid and its derivatives are used as constituents of some rubefacient products, for example, methyl salicylate is used as a liniment to soothe joint and muscle pain, choline salicylate is used typically to relieve the pain of aphthous ulcers [4]. Pyridine is simple aromatic heterocyclic organic compound with chemical formula (C_5H_5N) pyridine was industrially produced by extraction coal tar, it is currently synthesized from formaldehyde, ammonia and acetaldehyde it is harmful if inhaled swallowed or absorbed through the skin [5]. Effect of pyridine in toxication include dizziness headache, nausea and loss of appetite [6,7]. Pyridine is readily degraded by bacteria to ammonia and carbon dioxide.[8] The nitrogen atom on pyridine features a basic lone pair of electrons because this lone pair is not delocalized into the aromatic pi-system pyridine is widely used as a ligand in coordination chemistry [9, 10]. In this work pyridine and salicylic acid were used as ligands with some metal ions.

Experimental

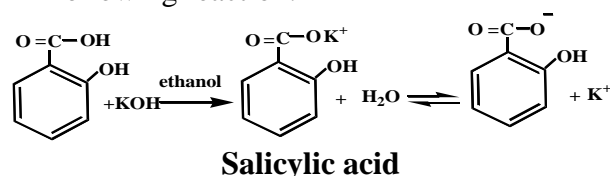
a- Materials and Measurements:

Metal salts ($MnCl_2.4H_2O$, $FeSO_4.2H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2$ and $HgCl_2$) were obtained from Fluka, in high purity.

The Ligand (Salicylic acid) (SA) from (BDH) and Pyridine (Py). Conductivity measurements were carried out using Philips Pw.Digital-Meter. The IR spectra in the range ($4000-400cm^{-1}$) were recorded using (Shimadzu FT-IR-8400), uv-visible spectra were measured in ethanol using (Shimadzu- uv-visible 160A).

b-General Method for Synthesis:

(1) Salicylic acid (SA) was deprotonated at room temperature. According to the following reaction:



(2) Synthesis of Complexes: Ethanolic solution of the metal salts, were added to the solution of the ligand (SA^-) in ethanol using stoichiometric amounts (1:2) (Metal: Ligand). The mixtures were stirred for two hours at room temperature, products were separated by adding excess of pyridine (4.5-1 ml). By treating the solutions with diethyl ether until complete precipitation, the precipitates were crystallized from ethanol and dried at $50^\circ C$.

Results and Discussion

The isolated complexes were crystallized in some common solvents such as DMSO, Ethanol and DMF. The conductivity measurements in DMSO indicated the non-electrolyte behavior, the metal determination were found to be in a good agreement with calculated values as in table (1) which includes

the physical properties, elemental analysis for these complexes. The analytical data confirmed the (1:2:2) (M:SA:Py) composition of the complexes.

a- Spectral studies:

Infrared spectra: In order to get further information about the coordination behavior of the ligand (SA) and (Py) with metal ions comparison of the infrared of free ligands and their complexes were made. Table (2) describes the important absorptions and assignments, the strong band at (3236 cm^{-1}) in the spectrum of the free ligand (SA) assigned to the $\nu(\text{OH})$, while another strong absorption band at (1658 cm^{-1}) could be explained as $\nu(\text{OCO})_{\text{asym}}$ where the $\nu(\text{OCO})_{\text{sym}}$ was noticed at (1442 cm^{-1})_{asym} [11-16]. The spectrum of free pyridine showed bands at (705 cm^{-1}) and (748 cm^{-1}) the assigned as (CH-out of plane def) and (out of- plane ring def) respectively but the band observed at (1610 cm^{-1}) assigned to $\nu(\text{C}=\text{N})$ [17]. The spectra of complexes exhibited marked differences in the absorption band belonging to the stretching vibration of $\nu(\text{O}-\text{H})$ of hydroxyl group have been found in the range of ($3245\text{-}3525\text{ cm}^{-1}$) shifted to higher frequencies by ($9\text{-}289\text{ cm}^{-1}$) suggesting the possibility of (SA^-) coordination through the oxygen atom at the hydroxyl group, absorption assigned for $\nu(\text{OCO})_{\text{sym}}$ was noticed at the range ($1446\text{-}1508\text{ cm}^{-1}$) shifted to higher position by ($4\text{-}66\text{ cm}^{-1}$) while the band caused by $\nu(\text{OCO})_{\text{asy}}$ appeared between ($1600\text{-}1635\text{ cm}^{-1}$) shifted to lower frequencies ($23\text{-}58\text{ cm}^{-1}$) which might indicates the coordination of the carboxylic group to the central metal ion. The stretching vibration band $\nu(\text{C}=\text{N})$ were observed in the rang ($1485\text{-}1600\text{ cm}^{-1}$) shifted to lower frequency by ($10\text{-}125\text{ cm}^{-1}$) which mean that the nitrogen atom of pyridine was involved in coordination [18]. Metal-nitrogen and M-Oxygen bands were further confirmed by the presence of the stretching vibrations of $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ around ($412\text{-}455\text{ cm}^{-1}$) and ($438\text{-}478\text{ cm}^{-1}$) respectively..

b- Electronic Spectra:

The absorptions and assignment related to the ligand and their complexes are listed in Table (3). The ligand, Fig.(3) exhibited an

absorption band in (UV) region at wave number (35587 cm^{-1}) which may be attributed to ($\pi \rightarrow \pi^*$) transition, other bands of low density appeared at (30395 cm^{-1}) was explained as ($n \rightarrow \pi^*$). Free pyridine showed absorption band in the (UV) region at (31250 cm^{-1}) which was expressed as the ($n \rightarrow \pi^*$) [19].

c- The spectra of complexes:

- $[\text{Mn}(\text{SA})_2(\text{Py})_2]$ (d^5):

This complex spectrum showed an absorption at (29069 cm^{-1}) which was assigned to (${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$) [20,21,22]

- $[\text{Fe}(\text{SA})_2(\text{Py})_2]$ (d^6):

Two absorption bands noticed at (30769 cm^{-1}) and (23430 cm^{-1}) explained as (C.T) and (${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$) respectively. [23].

- $[\text{Co}(\text{SA})_2(\text{Py})_2].6\text{H}_2\text{O}$ (d^7):

The spectrum of this complex exhibited the following bands at (33670 cm^{-1}), (23809 cm^{-1}) (16129 cm^{-1}) and (12658 cm^{-1}) which can be assigned as (C.T) (${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g(\text{P})}$), (${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$) and (${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$) respectively [24].

- $[\text{Cu}(\text{SA})_2(\text{Py})_2]$ (d^9):

The spectrum Fig.(4) of this complex gave two bands at (31055 and 13550 cm^{-1}) which can be assigned as (C.T) and (${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$) transition respectively [25].

- The white complexes $[\text{Zn}(\text{SA})_2(\text{Py})_2].6\text{H}_2\text{O}$, $[\text{Cd}(\text{SA})_2(\text{Py})_2].6\text{H}_2\text{O}$ and $[\text{Hg}(\text{SA})_2(\text{Py})_2].5\text{H}_2\text{O}$, where the electronic configuration of the metal is (d^{10}) confirms the absence of any ($d \rightarrow d$) transition [26].

According to spectral data as well as those obtained from elemental analysis. The chemical structure of complexes may be suggested as octahedral for

$[\text{M}(\text{SA})_2(\text{py})_2].x\text{H}_2\text{O}$.

$\text{M}^{+2} = (\text{Mn}, \text{Fe}, \text{Co}, \text{Cu}, \text{Zn}, \text{Cd}, \text{Hg})$.

$X = 0, 0, 5, 0, 5, 6, 6$.

(SA)⁻ = (Salicylato), (Py) = (Pyridine)

Table (1)
Physical properties of the complexes.

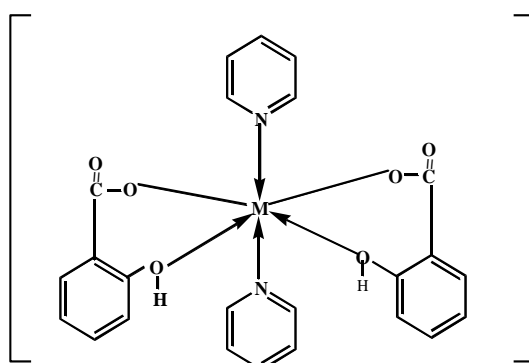
<i>Compounds</i>	<i>Color</i>	<i>M.P C°</i>	<i>M% calculated found</i>	<i>Am (ohm⁻¹.cm² Mol⁻¹) in DMSO 10⁻³ M</i>
(SA) ligand	White	159 -156	–	–
[Mn(SA) ₂ (Py) ₂]	White	275 -270	11.32(10.70)	11
[Fe(SA) ₂ (Py) ₂]	Yellow	200 -195	11.4 (11.37)	14.3
[Co(SA) ₂ (Py) ₂].5H ₂ O	Violet	285 -280	9.87 (8.61)	12
[Cu(SA) ₂ (Py) ₂]	Blue	165 -160	12.87(13.31)	10.5
[Zn(SA) ₂ (Py) ₂].5H ₂ O	White	180 -175	11.16 (11.68)	18
[Cd(SA) ₂ (Py) ₂].6H ₂ O	White	242 -235	17.28 (17.05)	20
[Hg(SA) ₂ (Py) ₂].6H ₂ O	White	255 -250	27.15 (26.90)	13

Table (2)
The characteristic infrared of salicylic acid (SA), pyridine and their metal complexes.

<i>Complexes</i>	<i>C=N</i>	<i>v(O-H)</i>	<i>v(OCO)_{asym}</i>	<i>v(OCO)_{sym}</i>	<i>v(M-N)</i>	<i>v(M-O)</i>
Ligand(SA)	–	3236	1658	1442	–	–
Pyridine	1610	–	–	–	–	–
[Mn(SA) ₂ (Py) ₂]	1566	3379	1600	1454	424	466
[Co(SA) ₂ (Py) ₂].5H ₂ O	1554	3250	1616	1508	416	478
[Fe(SA) ₂ (Py) ₂]	1585	3255	1631	1489	455	474
[Cu(SA) ₂ (Py) ₂]	1570	3421	1624	1450	412	438
[Zn(SA) ₂ (Py) ₂].5H ₂ O	1570	3245	1631	1485	424	470
[Cd(SA) ₂ (Py) ₂].6H ₂ O	1600	3448	1635	1489	420	470
[Hg(SA) ₂ (Py) ₂].6H ₂ O	1485	3525	1600	1446	420	447

Table (3)
The electronic Spectra for the free ligand and Its complexes ($10^{-3}M$).

Complexes	$\lambda_{max}(nm)$	ABS	Wave number (cm^{-1})	$E_{(max)}$ $L.M^{-1}$ cm^{-1}	Remarks
(SA).Ligand	281, 329	2.450, 1.661	35587 30395	2450 1661	$\pi \rightarrow \pi$ $n \rightarrow \pi^*$
Pyridine	320	1.09	31250	1090	$n \rightarrow \pi^*$
[Mn(SA) ₂ (py) ₂]	344	1.987	29069	1987	${}^6A_{1g} \rightarrow {}^4T_{2g}$
[Fe(SA) ₂ (py) ₂]	325 426.8	1.68 0.360	30679 23430	1680 360	C.T ${}^5T_{2g} \rightarrow {}^5E_g$
[Co(SA) ₂ (py) ₂].5H ₂ O	279 420 620 790	0.765, 0.200, 0.150 0.080	33670, 23809 16129, 12658	765, 200 150 80	C.T, ${}^4T_{1g(v3)} \rightarrow {}^4T_{1g(p)}$ ${}^4T_{1g(v2)} \rightarrow {}^4A_{2g}$ ${}^4T_{1g(v1)} \rightarrow {}^4T_{2g}$
[Cu(SA) ₂ (py) ₂]	322 738	2.362, 0.082	31055, 13550	2362, 82	C.T., ${}^2E_g \rightarrow {}^2T_{2g}$
[Zn(SA) ₂ (py) ₂].5H ₂ O	333	1.750	30030	1752	C.T
[Cd(SA) ₂ (py) ₂].6H ₂ O	266	2.50	37597	2520	C.T
[Hg(SA) ₂ (py) ₂].6H ₂ O	266	2.488	37597	2488	C.T



M = Co, Mn, Fe, Cu, Zn, Cd, Hg

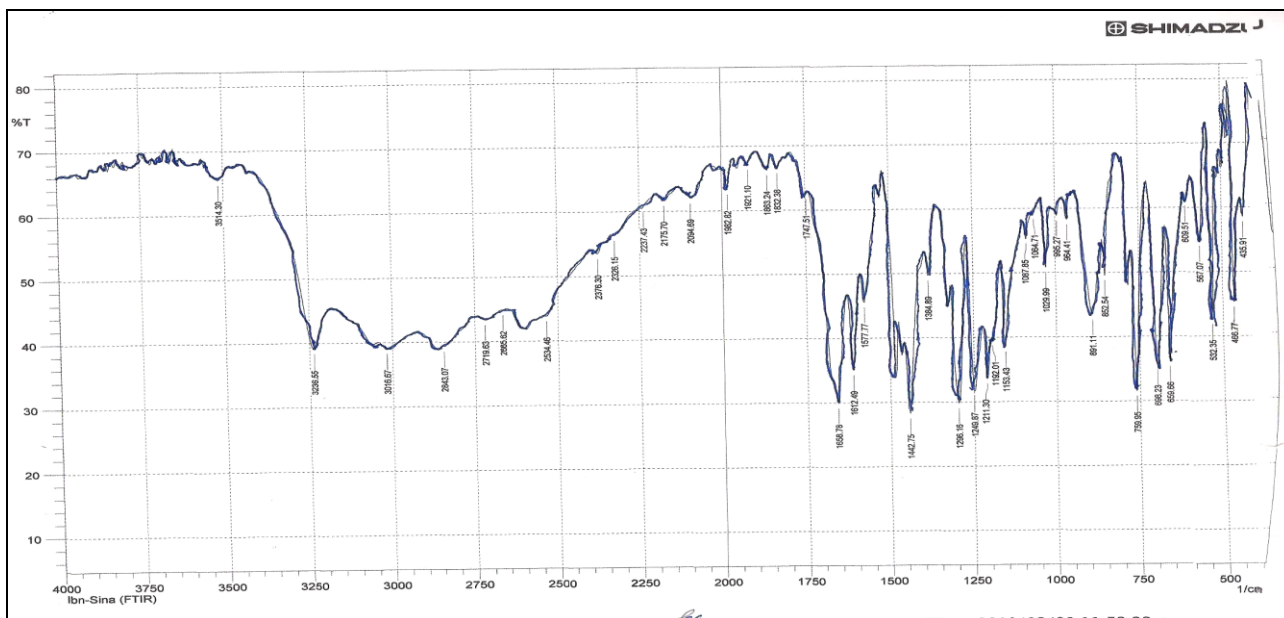


Fig.(1) Infrared (FT-IR of salicylic acid.

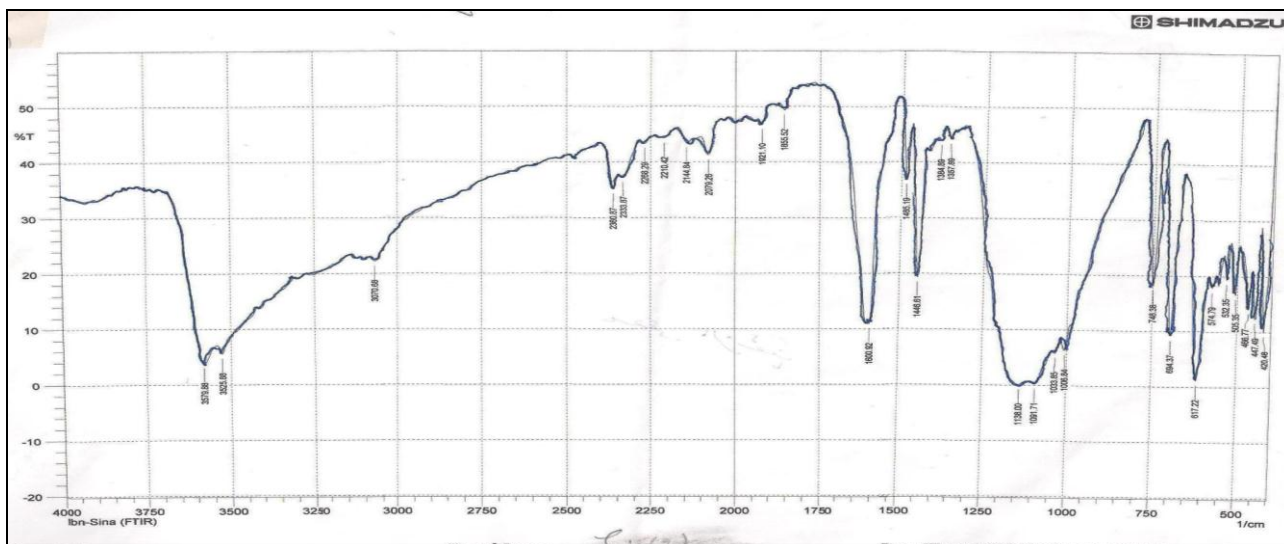


Fig.(2) Infrared of complex [Hg(SA)₂(Py)₂].6H₂O.

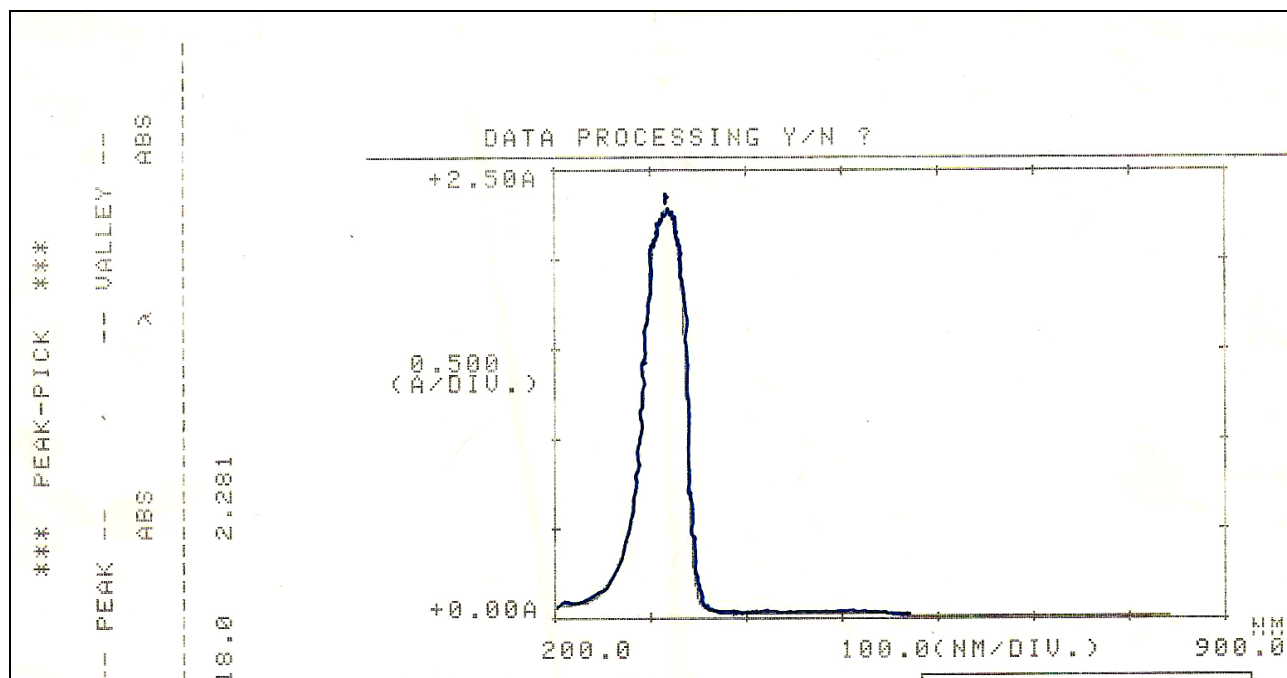


Fig.(3) UV-Visible of salicylic acid.

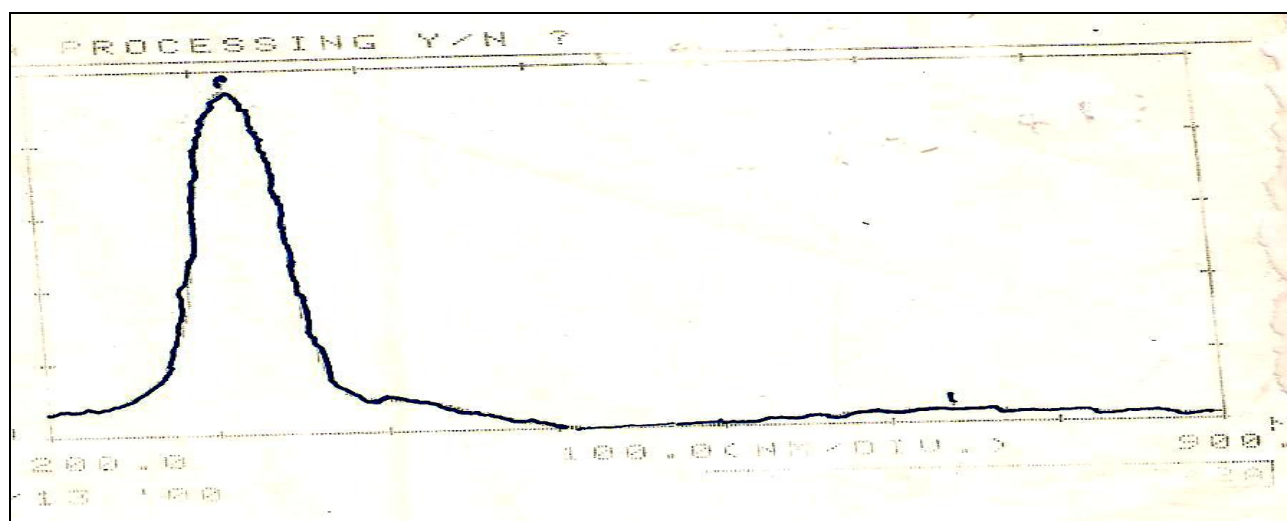


Fig. (4) UV-Visibl of complex[Cu(SA)₂(Py)₂].

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الخلاصة

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تضمن هذا البحث تحضير وتشخيص بعض المعقدات الفلزية التي تحوي على ليكاندات مختلفة لحامض السالسليك والبيريدين، وقد تم دراسة هذه المعقدات بالطرق الطيفية (الاشعة تحت الحمراء، الاشعة المرئية -الفوق البنفسجية) وتعيين نسبة الفلز في المعقدات بطريقة الامتصاص الذري، وكذلك تم قياس التوصيلية المولارية للمعقدات، ومن نتائج هذه الدراسات التشخيصية امكن اعطاء الصيغة العامة لهذه المعقدات $[M^{++}(SA)_2(Py)_2].XH_2O$ ، حيث $M =$ الايون الفلزي $(Mn^{+2}, Fe^{+2}, Co^{+2}, Cu^{+2}, Zn^{+2})$ $X =$ (Cd^{+2}, Hg^{+2}) ، $SA =$ (SA^-) ، $0,0,5,0,5,6,6 =$ بيريدين (py)، $(salicylato)$ الليكاند