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Some Metal Ions Complexes Derived From Schiff Base Ligand with Anthranillic Acid: Preparation, Spectroscopic and Biological Studies

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Abstract:

This search includes the preparation of Schiff base ligand (SB) from condensation primary amine with vanillin. The new ligand was diagnosed by spectroscopic methods as Mass, NMR, CHN and FTIR. Ligand complexes were mixed from new (SB) and Anthranillic acid (A) with five metal (II) chlorides. The preparation and diagnosis were conducted by FTIR, CHN, UV-visible, molar conductivity, atomic absorption and magnetic moment. The octahedral geometrical shape of the complexes was proposed. The ligands and their new complexes were screened with two different types of bacteria.

Key words: Anthranillic Acid, Geometrical, Mixed Ligands, Spectroscopy.

Introduction:

Mixed ligand complexes are very different conventional complexes in the sensation that have at least two various types of ligands linked with the same metal ion. One type of ligand in the compound increases the chances of variation in the expected properties of the compound. The synthesis and characterization of mixed ligaments are important day by day. The growing interest in this field of research has prompted many researchers to be engaged in this field (1-4). Perazole ring compounds cracks have been shown to be imported biological abilities (5). The primary amine of research is considered to be a heterogeneous ring compounds containing the pyrazol ring interacted with Benzoic aldehyde, then followed by dimerization(6). In this research, we characterized and description of the mixed coordination complexes of the ligands (Schiff base SB and anthranilic acid) with several metal ions.

Materials and Methods:

The starting materials and solvents used were of greatest purity (BDH, Fluka, merck) and used without moreover purification Metal contents of five complexes and melting points were obtained by using "Shimadzu AA 620G" and "Stuart melting point apparatus" in University of Tehran, the NMR

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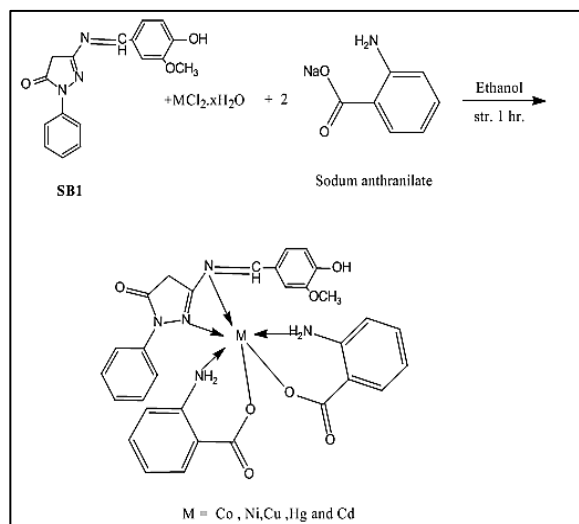
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and mass spectra were performed on by "Bruker DRX system 500 (500 MHz)" and Shimadzu, E170Ev. Elemental micro analysis "C, H, N and S" was carried out by the Euro EA 3000, University of Tehran. UV-Vis spectra were performed on a "Shimadzu UV- 160A". The FTIR- spectra were carried out by a "Shimadzu, FTIR- 8400S" (4000-400) cm^{-1} with samples prepared as KBr discs. Magnetic measurements were recorded on a "Bruker BM6 instrument" at 298K following the Faraday's method

Experimental:

Preparation of (Z)-3-(4-hydroxy-3-methoxybenzylideneamino)-1-phenyl-1H-pyrazol-5(4H)-one (SB): One mmol of (3-APP 0.173g) was dissolved in minimum quantity of ethanol and added drop by drop to ethanolic solution of vanillin (1mmol, 0.152g) with continuous stirring and it was refluxed on water bath about one day, yellow colored resulted and filtered off, then it was washed and dried. Yield was 81%, C (66.01%), H(4.89%) , N(13.58 %) and O(15.52%).

Preparation of Mixed Ligand Metal(II) complexes: Mixed solution of SB (0.309 g, 1mmole) and sodium anthranilate (0.274g, 2mmole) in ethanol (5ml) were added to one mmole stirred of various solution, 5ml of metal (II) chloride as $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and HgCl_2 . The complexes were stirred for one hour then filtered, and then dried, (Scheme. 1).



Scheme1. Preparation rout of complexes

Biological Activity: The Schiff base and their metal compounds were investigated with two bacteria like, *Escharia coli*, *Staphylococcus aureus* by disc diffusion technique. The complexes solutions used

in the biological study with dimethyl sulfoxide (DMSO) as solvent and they were provided as single concentration of 0.001M. The dishes were incubated at room temperature for one day. Inhibition areas grew in mm after a one day as a standard for the thickness of the effect of an artificial chemical compound on the growth of specific bacterial strains planted (7).

Result and Discussion:

In the present study, the physical and analytical properties for the Schiff base (SB), anthranillic acid (A) ligands and their complexes are presented in (Table 1). Five complexes were insoluble in H₂O, while soluble in (DMSO and DMF) solvent. Conductivity measurement data shows that all complexes are non-electrolytes in range (19.4-12.8) Ω⁻¹cm²mol⁻¹ in DMSO (0.001molar). The values found and the theories of M% ratio in each compound are in good agreement.

Table1: Physical and Analytical Information for All Compounds

Compounds	M.wt	Color	Yield	Melting point °C	\wedge_m	Metal % Found (Calc.)
SB	309	Yellow	81	125-127	-----	-----
A	137	Off-white	---	146-148	----	-----
[Co (SB)A ₂]	640	Brown	77	185-187	13.4	9.35(9.20)
[Ni (SB)A ₂]	640	Dark orange	75	210-212	14.6	9.78(10.94)
[Cu (SB)A ₂]	645	Greenish yellow	80	180-182	19.4	9.98(9.85)
[Cd (SB)A ₂]	693	White	69	218-220	12.8	15.80(16.20)
[Hg (SB)A ₂]	783	Yellow	78	197-199	15.6	25.88(25.65)

Mass Spectrum of SB: ligand SB spectrum is shown in (Fig.1), the M.wt ion peak for

(C₁₈H₁₈N₄O) ligand equal 309.32 m/z which were very much steady with the theoretical value (8).

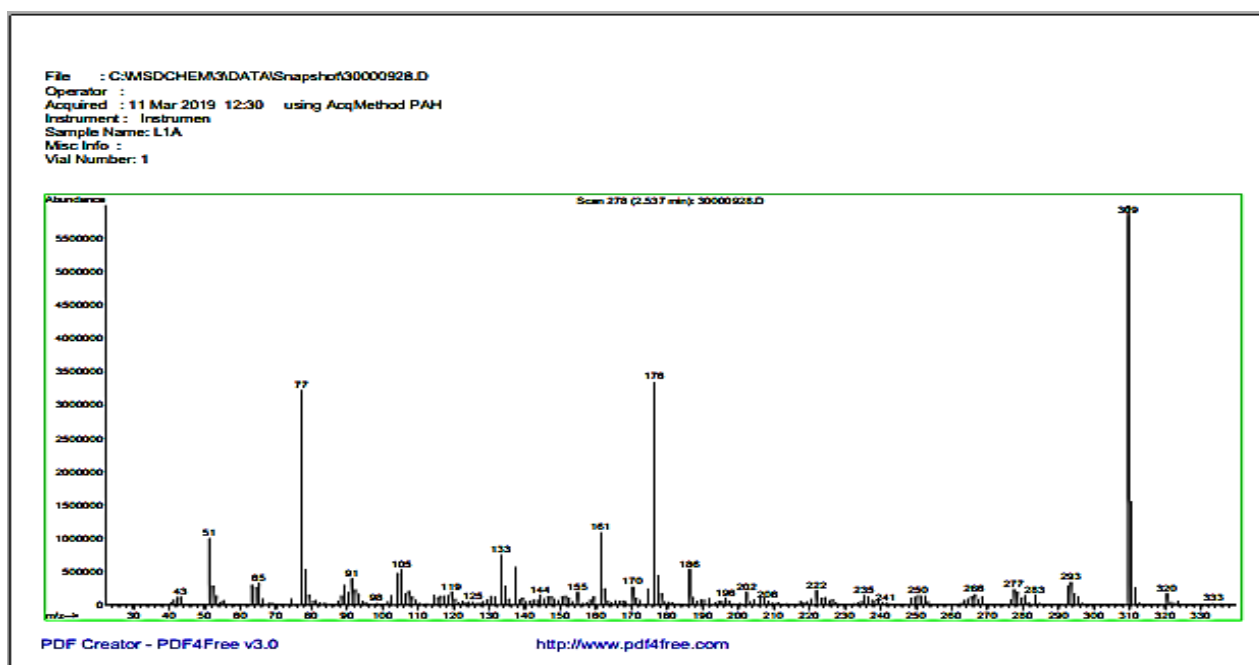


Figure1. Mass for SB ligand

¹H-NMR Spectrum of SB Ligand: The spectrum of the prepared ligand SB solvent in DMSO-*d*₆ is shown in (fig.2). The singlet signal in δ (2.49, 2.53) ppm may be attributed to the solvent and (-CH₂) of pyrazol ring respectively (9). The multiple signals

ranged between δ (6.25-7.75) ppm were assigned to the aromatic protons, and the singlet signal at δ (8.94 and 9.76) ppm was due to the azomethine and OH protons (10,11).

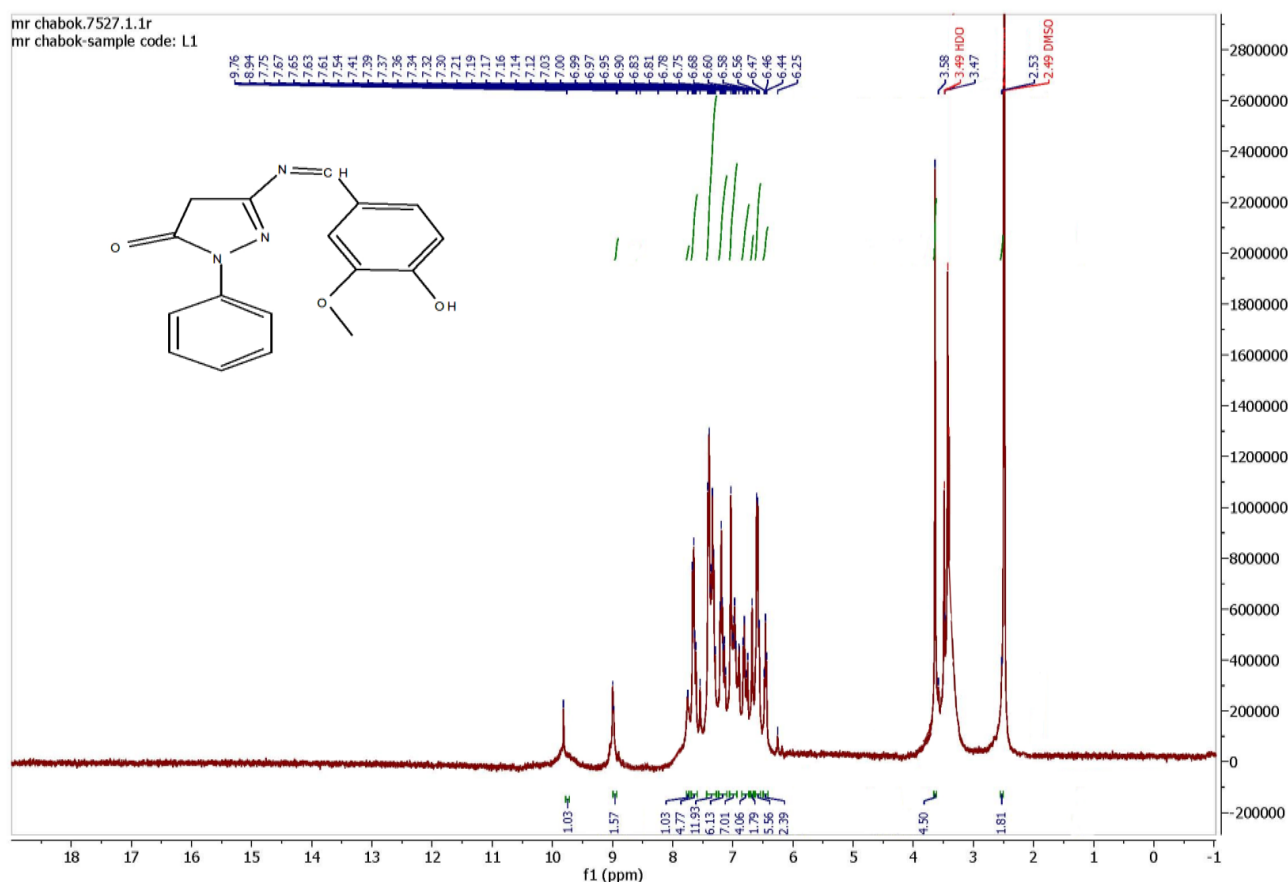


Figure 2. ¹H-NMR spectrum of SB ligand

FTIR Spectrum: Schiff base ligand showed bands at (3456, 1693, 1597 and 1627) cm⁻¹ which were attributed to the (O-H aromatic, -CO, -CN- pyrazol ring and Schiff base group) stretching vibration respectively (12), (Table 2) (Fig. 3). The spectrum of (A) showed bands at 3390, (3344_{asy.} 3244_{sym.}) and (1679_{asy.}, 1486_{sym.}) cm⁻¹ which are attributed to ν (-OH, -NH₂ and -COO). In the spectra of the complexes, the shifting was observed in stretching vibration for Schiff group and imine pyrazol ring to the lower frequency at (1616-1612) cm⁻¹ and (1589-1581) cm⁻¹ compared to the free ligand spectrum. This shifting in the site of the bands is credible guide of the connected between the N atom in these

groups and the metal ion (13, 14). The association of the carboxyl group is a mono-dentate donor and for this reason absorption bands (COO)_{asy., sym.} in these complexes shifted to lower frequencies for ν(COO)_{asy.} at (1581-1523) cm⁻¹ and ν(COO)_{sym.} at (1377-1315) cm⁻¹ and the variance between Δ_{asy-sym} was (216-208) cm⁻¹ (15). FTIR spectra complexes showed the new absorption bands at (520-505 and 559-516) cm⁻¹ and (439-408) cm⁻¹, it could prove the coordination metal-N for SB ligand, amine of amino acid groups and metal-O respectively (16-18). The absorption bands of the complexes which ranged between (1696-1992) cm⁻¹ and were assignable to ν (CO) pyrazol ring (19-21).

Table 2. FTIR Spectra for the prepared compounds and Anthranillic acid

Comp.	OH(SB) N-H ₂ asy & sym	COO asy & sym	Δ asy- sym	CN Schiff	C=O	CN _{py}	M-N Sch. Anth.	M-O
SB	3456 ---	---	----	1627	1693	1597	----	----
A	3390 3344-3244	1679 1486	193	-----	----	-----	----	----
[Co(SB)A ₂]	3305-3244	1543 1327	216	1612	1695	1585	505 559	439
[Ni(SB)A ₂]	3437-3305	1543 1327	216	1612	1692	1581	520 532	420
[Cu(SB)A ₂]	3444-3275	1581 1377	204	1612	1696	1581	505 516	428
[Cd(SB)A ₂]	3417-3294	1539 1337	212	1616	1695	1589	516 582	408
[Hg(SB)A ₂]	3336-3325	1523 1315	208	1612	1694	1581	509 520	432

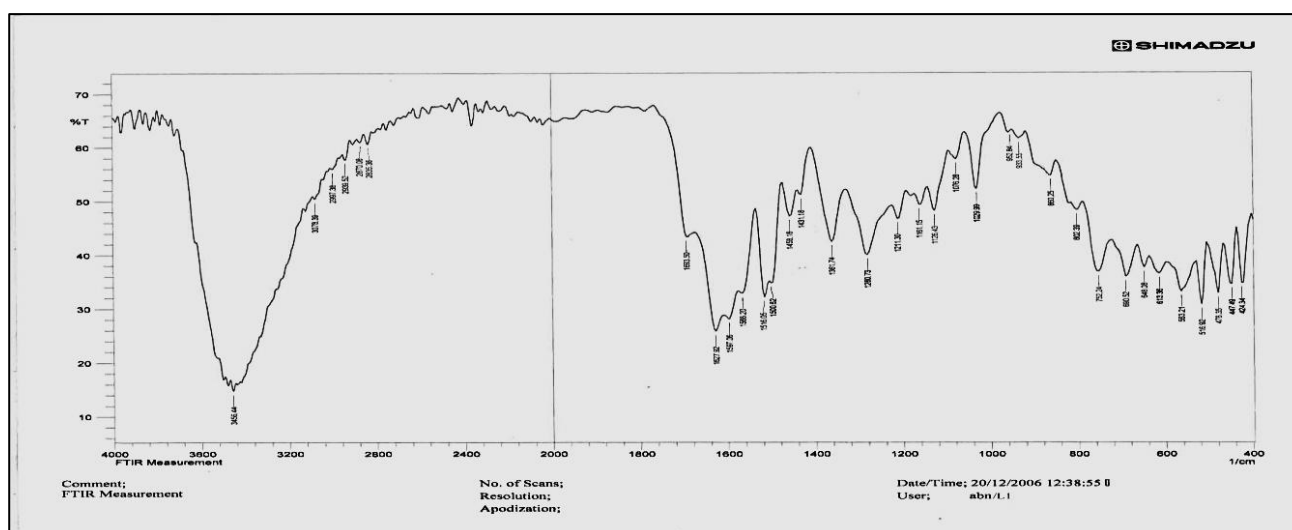


Figure 3. FT-IR Spectrum of SB Ligand

Electronic Spectral: The UV-Vis. Spectrum of ligand SB showed three peaks, the first in (289 and 390)nm were due to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) respectively (table3) (22-25). The [Co (SB)A₂] spectrum showed various peaks, three peaks at (277, 350 and 397)nm which were attributed to intra ligand and charge transfer respectively. The other peaks at 500nm, (652, 709 nm) and 813nm were assigned to d-d electronic transition as shown in the Table 3. These peaks were at good agreement of octahedral geometry for cobalt complex (26). [Ni (SB)A₂] spectrum was appeared number of transitions, the peaks at (275,350)nm and 394 nm were attributed to intra ligand and charge transition respectively. Other new peaks at 489, (777,862) nm and 958 nm are due to type d-d transitions, Table 3. These peaks indicate that the nickel complex takes octagonal shape (26). [Cu (SB)A₂] spectrum

displayed four absorption peaks, the two absorption peak at [297, 314 , 345 , 495 and 693] nm are due to intra ligand, charge transfer and d-d respectively as shown in Table 3. These peaks are an evidence that the copper complex takes octagonal geometry .The UV-Vis spectrum of Hg and Cd complexes, absorption peaks shown at (272, 332,346,395 and 463) nm and peaks at (265, 325 and 401) nm are assigned to intra ligand and charge transfer (C.T) respectively. These peaks are an evidence that the mercury and cadmium complexes take octagonal geometry (27).

Measurement of Magnetic Complexes: the μ_{eff} of Co⁺², Ni⁺² and Cu⁺² complexes were (3.9, 2.85 and 1.72) B.M respectively, these values indicate an octahedral geometry around three metal ions (Table 3)(26).

Table 3. The Electronic Spectrum of Prepared Compounds

Compound	λ nm(cm^{-1})	Type of transitions	μ_{eff} (BM)
SB	289(34602) 390(25641)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	---
[Co (SB) A ₂]	277(36101) 350(28471) 397(25188) 500(20000) 652,709(15337,14104) 813(12300)	Intra-ligand Intra-ligand C.T. $^4T_1g(F) \rightarrow ^4T_1g(P) \nu_3$ $\rightarrow ^4A_2g(F) \nu_2$ $\rightarrow ^4T_2g(F) \nu_1$	3.9
[Ni (SB) A ₂]	275(36363) 350(28571) 394(25380) 489(20449) 777,826(12870,12106) 958(10438)	Intra-ligand Intra-ligand C.T. $^3A_2g(F) \rightarrow ^3T_1g(P) \nu_3$ $\rightarrow ^3T_1g(F) \nu_2$ $\rightarrow ^3T_2g(F) \nu_1$	2.85
[Cu (SB) A ₂]	275,314(36363,31847) 345(28985) 423(23640) 693(14430)	Intra-ligand Intra-ligand C.T. $^2Eg \rightarrow ^2T_2g$	1.72
[Cd (SB) A ₂]	265(37735) 325(30769) 401(25937)	Intra-ligand Intra-ligand C.T.	Dia.
[Hg (SB) A ₂]	272,332(36764,30120) 346,395(28901,25316) 463(21598)	Intra-ligand Intra-ligand C.T.	Dia.

Study of Antibacterial Activity: Five complexes and two ligands were tested against two types of bacteria gram positive and gram negative by utilizing plate method in nutrient agar (28, 29). The diameter of the inhibition for the bacterial medium growth of the complexes was listed in the Table 6. The study showed that the prepared compounds of ligand SB, Anthranillic acid, [Co(SB)A₂] [Ni(SB)A₂], [Cu(SB)A₂], [Hg(SB)A₂] and [Cd(SB)A₂] were different efficacy against *E.coli* and *Staphylococcus aureus* (Table4 and Fig. 1).

Table 4. The inhibition for the bacterial growth of the compounds

Compounds	<i>Escharia coli</i>	<i>Staphylococcus</i>
DMSO	-	-
SB	11	-
A	18	21
[CoA ₂ SB]	14	24
[NiA ₂ SB]	-	10
[CuA ₂ SB]	28	19
[CdA ₂ SB]	18	32
[HgA ₂ SB]	32	29

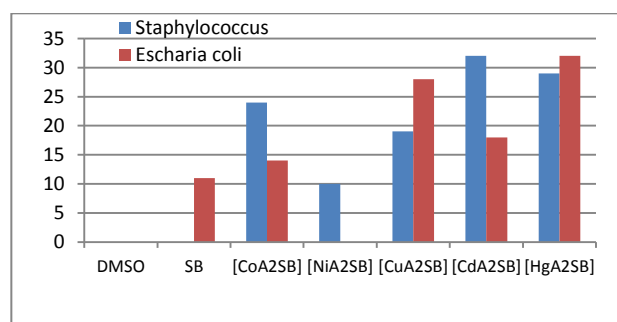


Figure 1. biological activity for prepared compounds against different bacteria

Conclusions:

The new Schiff base derived from primary amine with vanillin was synthesized and characterized. The results showed that Schiff base ligand format with metal ions through the two N were as donor atoms. The results of the electron spectra and the magnetic susceptibility of octahedral geometry of all complexes were given. The composite compounds were studied as antimicrobial and the results showed that all complexes have a various activities against bacteria.

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Conflicts of Interest: None.

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بعض معقدات الايونات الفلزية المشتقة من ليكاند قاعدة شف و حامض الانثرائيلك : تحضير و دراسات الطيفية والفعالية البايولوجية

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الخلاصة:

يتضمن هذا البحث تحضير ليكاند قاعدة شف SB من تكثيف 3-امينو- 1- فنييل -2- بيرزولين -5- اون مع الفانلين. شخص الليكاند الجديد بواسطة الطرق الطيفية مثل طيف الكتلة وطيف الرنين النووي المغناطيسي و التحليل الدقيق للعناصر و الاشعة تحت الحمراء والاشعة فوق البنفسجية. حضرت وشخصت معقدات مختلطة الليكاند من ليكاندات SB و حامض الانثرائيلك (A) مع خمس من كلوريدات العناصر (II) بواسطة الاشعة تحت الحمراء، التحليل الدقيق للعناصر، الاشعة فوق البنفسجية والمرئية، التوصيلية المولارية، الامتصاص الذري، الحساسية المغناطيسية. تم اقتراح الشكل الثماني السطوح للمعقدات. تم فحص الليكاندات والمعقدات الجديدة ضد نوعين مختلفين من البكتيريا.

الكلمات المفتاحية: حامض الانثرائيلك والهيئة وليكاندات مختلطة مطيافية.