

Synthesis, Characterization and Study the Mixed Ligand Complexes of (L-alanine and Saccharin) with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) ions

**تحضير، تشخيص ودراسة المعقدات مختلطة الليكاند من
(الالانين و السكرين) مع أيونات Mn(II), Fe(II), Co(II), Ni(II), Cu(II)**

Maysoon Abd Al-Hussein Al-Soodani
University of Al-Mustansiriya

Abstract

The research includes the synthesis and identification of two mixed ligands complexes of some heavy metal ions by using the amino acid (L-alanine), as a primary ligand and (Saccharin) as secondary ligand. The general formula of the complexes is $Na_2[M(Ala)_2(Sac)_2]$ in which the L-alanine ($C_3H_7NO_2$) is symbolized as (Ala) and Saccharin ($C_7H_5NO_3S$) is symbolized as (Sac). The reaction is established by reacting the two ligands with the metal chloride by using ethanol as solvent at temperature ($80^\circ C$) with the molar ratio [(1:2:2) (M:L₁:L₂)] where:

M(II)= Mn(II), Fe(II), Co(II), Ni(II) and Cu(II), L₁= Sac⁻, L₂= Ala⁻.

L-alanine behaves as a bidentate ligand, which is coordinated through the oxygen atom of the carboxyl group ($-COO^-$), and the nitrogen atom of the amino group (NH_2), while saccharin behaves as a monodentate ligand, which is coordinated through the nitrogen atom.

الخلاصة

يتضمن البحث تحضير وتشخيص المعقدات مختلطة الليكاند مع بعض الايونات الفلزية الثقيلة باستعمال الحامض الاميني (الالانين) ليكاند أولي و (السكرين) ليكاند ثنائي. والصيغة العامة للمعقدات هي: $Na_2[M(Ala)_2(Sac)_2]$ إذ ان الالانين ($C_3H_7NO_2$) بالرمز (AlaH) والسكرين $C_7H_5NO_3S$ بالرمز (SacH) وذلك بمفاعلة الليكاندين مع كلوريد العناصر باستعمال الايثانول مذيباً وفي درجة حرارة ($80^\circ C$) وبنسبة مولية [(1:2:2) (M: L₁:L₂)] حيث أن:

M(II) = Mn(II), Fe(II), Co(II), Ni and Cu(II), Sac⁻ = $C_7H_4NO_3S^-$, Ala⁻ = $C_3H_6NO_2^-$

يسلك الليكاند حامض الالانين [(الفائد بروتون والمتحول إلى أيون الالانينت (Ala⁻)] باستعمال القاعدة (NaOH) كليكاند ثنائي السن، إذ يرتبط بالأيون المركزي عن طريق ذرة الأوكسجين في مجموعة الكاربوكسيل ($-COO^-$) وذرة النتروجين في مجموعة الأمين (NH_2) بينما يسلك السكرين كليكاند أحادي السن إذ يرتبط من خلال ذرة النتروجين.

Introduction

Saccharin (or o-sulphobenzoimide) is widely used as an artificial sweetener. The chemistry of saccharin has attracted attention because of its suspected carcinogenous nature [1,2]. The saccharin molecule contains a set of donor atoms that are able to bind metal ions [3].

Studying the coordination nature of saccharin and determining the binding site (s) to metal ions is perhaps a key to understand the bioinorganic chemistry of saccharin [4-7]. Saccharin (Figure1) was discovered by Remsen and Fahlberg in 1879 [8]. In Chemical Abstracts, besides the conventional name, saccharin appears as **1,2-benzisothiazole-3(2H)-one-1,1-dioxide** [9]. Saccharin is about 500 times sweeter than sugar [10].

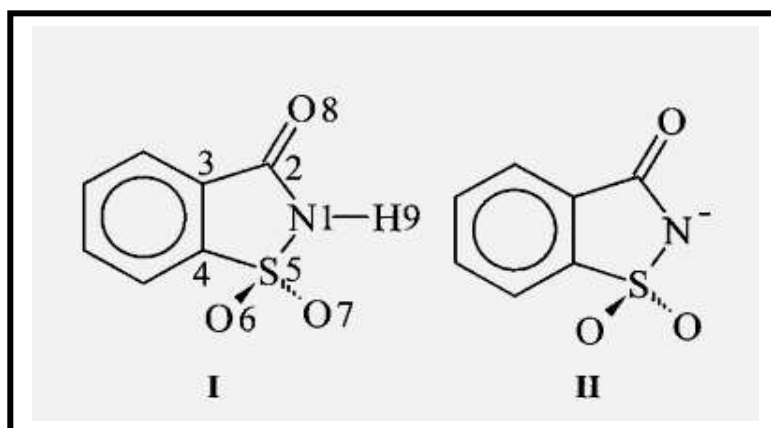


Figure (1): Saccharine (I) and saccharinato anion (II)

The saccharine complexes of Au(III), ZrO(II), VO(II) and UO₂(II) metal ions have been prepared and the coordination of saccharin in these complexes has been investigated through their ¹H NMR and IR spectra as well as by thermal analysis. It was found that saccharin reacts with all of these metal ions in the anionic form and coordinated in a monodentate fashion through its nitrogen atom with Au(III), ZrO(II) and VO(II) ions. A square planar shape has been proposed for Au(III) complexes, polymeric chain shapes for ZrO(II) and VO(II) complexes and an octahedral structure for UO₂(II) saccharin complex [11].

All the divalent cations of the first transition metal series (V-Zn) show a clear preference to interact with the saccharinate anion through its deprotonated N atom, generating tetra aqua bis (saccharinate) complexes, [M^{II}(sac)₂(H₂O)₄], with the saccharinate ligands in *trans* position [12-15].

The characterization and quantitative investigation of the binding properties of amino acids towards transition metal ions plays an important role in our understanding of metal-protein interactions [16]. Metal amino acid complexes have long been of interest as models for metal-ligand systems and interaction which may occur in nature [16,17].

L-alanine is one of the twenty major amino acids and is considered an essential amino acid besides the conventional name alanine appears as (S)-2-aminopropanoic acid [18].

The present investigation deals with the preparation, spectroscopic studies and structural of complexes of M⁺² ions using amino acid (alanine) as a primary ligand and Saccharin as a secondary ligand.

Experimental Section:

1- Materials:

All of the chemical used throughout this investigation were extra pure grade. Chemicals Saccharin, L- alanine, and metal salts were purchased from Merck and BDH were used without further purification.

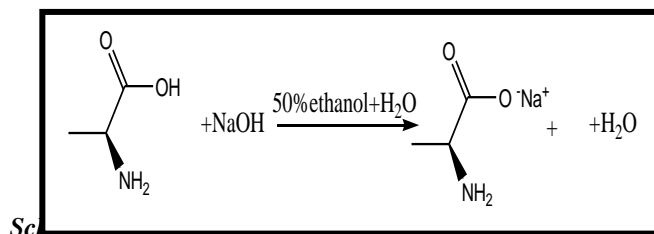
FT- I.R spectra were recorded as **KBr** discs using Fourier Transform Infrared Spectrophotometer Shimadzu 24FT-IR8300. Electronic spectra of the prepared complexes were measured in the region (200- 1100)nm for 10⁻³ M solutions in DMF at 25°C using shimadzu-U.V-160 A Ultra Violet Visible- Spectrophotometer with 1.000 ± 0.001 cm matched quartz cell .Identify the metal percentage in the complexes by using Shimadzu flame atomic absorption Model;6809. Electrical conductivity measurements of the complexes were recorded at 25°C for 10⁻³ M solutions of the samples in DMF using pw 9527 Digital conductivity meter (Philips).Melting points were recorded by using Stuart melting point apparatus. Chloride ion content were also evolution by (Mohr method), Magnetic susceptibility measurements were measured using Bruker magnet BM6. The

proposed molecular structure of the complexes were determined by using chem. office 2006, 3DX program.

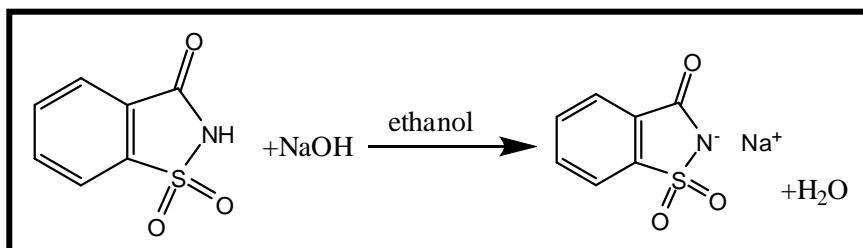
2-Method:

a- Preparation the ligands to coordinate:

1) **Sodium alaninate**:- dissolve [1.68gm(2mmol)] of alanine with [0.08 gm (2mmol)] solution of sodium hydroxide in 50% ethanol was deprotonated according to the following reaction .Scheme (1)



2) **Sodium saccharinate**:- dissolve [3.66gm(2mmol)] of saccharin with [0.08 gm (2mmol)] solution of sodium hydroxide in ethanol was deprotonated according to the following reaction . Scheme (2)



b- Synthesis of complexes:

The complexes were prepared by the addition of ethanolic solutions of the ($\text{Na}^+ \text{Sac}^-$) and ($\text{Na}^+ \text{Ala}^-$) to warm stirred ethanolic solution of the respective metal (II) chloride in the stoichiometric ratio (metal: ligands) ($\text{M}:(\text{Sac})_2:(\text{Ala})_2$) for (20 min). The mixture was stirred for half an hour at (80°C), crystalline precipitate observed. The resulting precipitate was filtered off and recrystallized from its ethanolic solutions then dried at 50°C .

Results and Discussion

All the complexes (Figure-2) are colored, non-hygroscopic and thermally stable solids (Table-1) indicating a strong metal-ligand bond. Physical properties are presented in (Table 1). The complexes are insoluble in water but soluble in common organic solvents such as ethanol, ethyl alcohol, acetone, chloroform, DMF and DMSO. The observed molar conductance (Table 1) values measured in DMF in 10^{-3}M solution lie in the $((129 - 178)) \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ range, indicating their electrolytic nature with (1:2) [19]. The atomic absorption measurements (Table-1) for all complexes gave approximated values for theoretical values.

The magnetic moments of the complexes shown in Table (2) were calculated from the measured magnetic susceptibilities after employing diamagnetic corrections [20,21].

The magnetic moments obtained at room temperature for the complexes of Cu(II), Ni(II) and Co(II) are listed (Table 2). Cu(II) complex exhibits magnetic moment (1.95 B.M), which is less than the normal value ($\sqrt{8} = 2.828$). The lowered magnetic moment value observed for Cu(II) complex under present study is due to distorted octahedral geometry [21]. The Co(II) complex shows magnetic moment of 4.86 B.M. the spin free octahedral complex are reported to exhibit magnetic moment in the range of (4.46- 5.53) B.M [20].

The Ni(II) complex shows magnetic moment of 2.69 B.M. octahedral. The magnetic moment of octahedral Ni(II) complex are reported to exhibit magnetic moment in the range of (2.80 – 3.40) B.M. (2.69) including spin orbital coupling contribution from $3A_{2g}$ and higher $3T_{2g}$ states. Hence the observed magnetic moment for the Ni(II) complex suggest that it may have octahedral geometry [22].

The electronic spectral data of the free ligands saccharin, L-Alanine and their complexes are summarized in (Table-2) figures (3-8) together with the proposed assignments and suggested geometries. The results obtained are in good agreement with other spectra and the literature [28].

The UV-Vis spectrum of the ligand (saccharin) shows peaks at 256 nm, 340 nm and 362 nm assigned to $(\pi - \pi^*)$ and $(n - \pi^*)$ electronic transitions. The spectrum of the free ligand (Ala-) in DMF shows two high intensity band in wave length 304nm (32894 cm^{-1}) ϵ max ($3911 \text{ mol}^{-1} \cdot \text{cm}^{-1}$) and 277nm. (36101 cm^{-1}) ϵ max ($3431 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) assigned to $(n \rightarrow \pi^*)$ and $(\pi \rightarrow \pi^*)$ transition respectively [22,23].

The Fourier transform infrared spectrum of free ligand saccharin (Hsac) Figure (10) exhibits a weak band at 3441 cm^{-1} due to the ν (N-H) vibration [24,25]. This band is not present neither in the spectra of its sodium salt nor of the saccharinato complexes. This observation suggests that saccharin reacted with these metal ions in the anionic form.

The region involving the carbonyl stretching vibrations is relatively complex, as both the C=O vibrations of saccharin and of the Imine group lie closely together, and of the NH_2 moiety are expected in the same region [26]. The $\nu(\text{C}=\text{O})$ mode of the saccharinate anion lies slightly lower than in sodium saccharinate (1589 cm^{-1}) in agreement with its participation in hydrogen bonding.

The two SO_2 -stretching vibrations appear at similar frequencies as in sodium saccharinate (1292 and 1150 cm^{-1} for $\nu_{\text{as}}(\text{SO}_2)$ and $\nu_{\text{s}}(\text{SO}_2)$, respectively [24-26]. The $\nu_{\text{as}}(\text{CNS})$ mode of saccharinate anion lies at (966 cm^{-1}) a higher frequency (918 - 956 cm^{-1}) than all complexes, figures (11- 1°) [23]. The complexes show band at (646 - 696 cm^{-1}) and (522 - 580 cm^{-1}) rang, due to the ν (M-N) and ν (M-O) vibrations respectively [24-27].

Proposed molecular structure:

Studying complexes on bases of the above analysis , the existence of hexa coordinated $[\text{M}(\text{C}_3\text{H}_6\text{NO}_2)_2(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2]^{-2}$, were $\text{M}=\text{Mn}(\text{II}), \text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ proposed models of the species were built with chem3D shows in Figur-2.

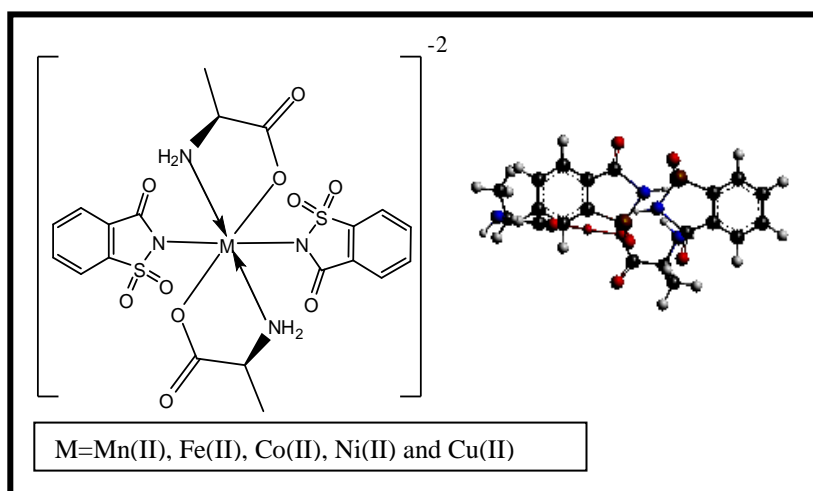


Figure 2: The suggested structure for the complexes $[\text{M}(\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_{10}\text{S}_2)]^{-2}$

Nomenclature of prepared complexes:

Table (3) shows empirical formula and nomenclature (IUPAC) with abbreviated.

Conclusion:

Thus the evidences obtained from IR spectra, electronic spectra and magneto chemical measurements suggest an octahedral structure (Figure. ۷) for metal (II) complexes in which alanine acts as a bidentate ligand and saccharin behaves as monodentate ligand.

Table (1): The physical properties of the complexes Na₂[M (C₂₀H₂₀N₄O₁₀S₂)]

Compound	M. wt	Color	M. p°C (de)°C	Λ _m in (1x10 ⁻³) DMF μS.cm ² .Mol ⁻¹	Metal%		C 1%
					theory	exp	
C ₃ H ₇ NO ₂ (L-AlaH)	89	White	222	1.3	-	-	-
C ₇ H ₅ NO ₃ S (SacH)	183.19	Off white	113	12.4	-	-	-
Na ₂ [Mn(C ₂₀ H ₂₀ N ₄ O ₁₀ S ₂)]	641.54	Pale pink	278 de	166	9.23	11	Nil
Na ₂ [Fe(C ₂₀ H ₂₀ N ₄ O ₁₀ S ₂)]	642.6	brown	250 de	143	9.36	10.5	Nil
Na ₂ [Co(C ₂₀ H ₂₀ N ₄ O ₁₀ S ₂)]	645.53	Pink/Red	232 de	178	9.83	10.3	Nil
Na ₂ [Ni(C ₂₀ H ₂₀ N ₄ O ₁₀ S ₂)]	645.31	green	244 de	131	9.80	11.1	Nil
Na ₂ [Cu(C ₂₀ H ₂₀ N ₄ O ₁₀ S ₂)]	650.14	Green/Blue	280 de	129	10.52	10.89	Nil

Λ_m = Molar Conductivity, de = decomposition

Table (2): Electronic Spectra data, magnetic moment, of the studied Complexes

Complexes	λ _{nm}	ν̄ (Cm) ⁻¹	μ _{eff} (BM)	Assignment	Probable figure
Na ₂ [Mn(Sac) ₂ (Ala) ₂]	251 271 658 776	39840 36900 15197 12886	5.24	L-F L-F ⁶ A _{1g} → ⁴ T _{2g} ⁴ A _{1g} → ⁴ T _{1g}	Distorted Octahedral
Na ₂ [Fe(Sac) ₂ (Ala) ₂]	299 351 895	33444 28490 11173	۰.29	L-F C-T ⁵ T _{2g} → ⁵ E _g	Distorted Octahedral
Na ₂ [Co(Sac) ₂ (Ala) ₂]	234 282 654 873	42735 35460 15290 11454	4.86	L-F L-F ⁴ T _{1g} → ⁴ T _{1g} ⁴ T _{1g} → ⁴ A _{2g}	Distorted Octahedral
Na ₂ [Ni(Sac) ₂ (Ala) ₂]	234 287 319 876	42735 34843 31347 11415	2.69	L-F L-F C-T ³ A _{2g} → ³ T _{1g}	Distorted Octahedral
Na ₂ [Cu(Sac) ₂ (Ala) ₂]	230 288 355 878	43478 34722 28169 11389	1.95	L-F L-F C-T ² E _g → ² T _{2g}	Distorted Octahedral

Table (3): Nomenclature of prepared complexes

<i>Complexes</i>	<i>Nomenclature</i>	<i>Abbreviation</i>
$\text{Na}_2[\text{Mn}(\text{C}_3\text{H}_7\text{NO}_2)_2(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2]$	Sodium di(L-alaninato)bis(saccharinato) manganate (II)	$\text{Na}_2[\text{Mn}(\text{Sac})_2(\text{Ala})_2]$
$\text{Na}_2[\text{Fe}(\text{C}_3\text{H}_7\text{NO}_2)_2(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2]$	Sodium di(L-alaninato)bis(saccharinato) ferrate(II)	$\text{Na}_2[\text{Fe}(\text{Sac})_2(\text{Ala})_2]$
$\text{Na}_2[\text{Co}(\text{C}_3\text{H}_7\text{NO}_2)_2(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2]$	Sodium di(L-alaninato)bis(saccharinato) cobaltate (II)	$\text{Na}_2[\text{Co}(\text{Sac})_2(\text{Ala})_2]$
$\text{Na}_2[\text{Ni}(\text{C}_3\text{H}_7\text{NO}_2)_2(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2]$	Sodium di(L-alaninato)bis(saccharinatato) neikelate (II)	$\text{Na}_2[\text{Ni}(\text{Sac})_2(\text{Ala})_2]$
$\text{Na}_2[\text{Cu}(\text{C}_3\text{H}_7\text{NO}_2)_2(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2]$	Sodium di(L-alaninato)bis(saccharinato) cupperate(II)	$\text{Na}_2[\text{Cu}(\text{Sac})_2(\text{Ala})_2]$

Table (4): FT-IR spectral data of the Ligands and there complexes

Compounds	$\nu(\text{N-H})_{\text{asy}}$ $\nu(\text{N-H})_{\text{sym}}$	$\nu(\text{CH})_{\text{alph}}$ $\nu(\text{C-H})_{\text{cy}}$	$n_{\text{asy}}(\text{SO}_2)$ $n_{\text{sym}}(\text{SO}_2)$	$n_{\text{asy}}(\text{CNS})$	$\nu(-\text{COO})_{\text{asy}}$	$\nu(-\text{COO})_{\text{sym}}$	M – N	M – O
Ala-H	3379m 3087m	2937s		-	1618 vs	1411 s	-	-
Sac-H	3402s 3113br-vs	- 2928vs-s	1292 vs 1178 vs	966s	-	-	-	-
$\text{Na}_2[\text{Mn}(\text{ Sac})_2(\text{Ala})_2]$	3088 vs 3016 s	2931s	1256 m 1151 s	918m	1620vs 1458s	1411s 1361vs	646m	540m
$\text{Na}_2[\text{Fe}(\text{Sac})_2(\text{Ala})_2]$	3394m 3090vs	2706m	1298 m 1166m	918m	1635m-1462s	1338s-	696m	522m
$\text{Na}_2[\text{Co}(\text{Sac})_2(\text{Ala})_2]$	3506-3103 vs	2939s	1290vs 1157 s	956s;	1622vs 1583vs	1356vs	673m	536m
$\text{Na}_2[\text{Ni}(\text{ Sac})_2(\text{ Ala})_2]$	3385vs	2322w	1294 m 1155m	952m	1626vs 1583vs	1346s	675m	547m
$\text{Na}_2[\text{Cu}(\text{Sac})_2(\text{Ala})_2]$	3441m 3290vs	3962vs-s	1294 m 1147s	923m	1616vs 1577vs	1338s	648m	580m

s= sharp, vs= very sharp, m= medium, br= broad

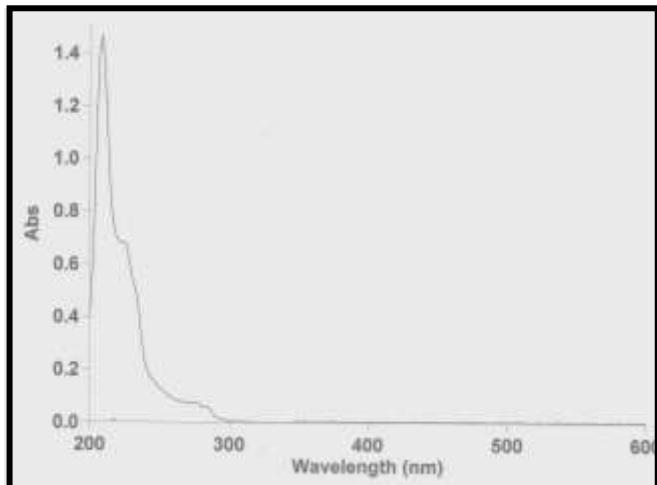


Figure (3): UV Spectrum of Saccharin

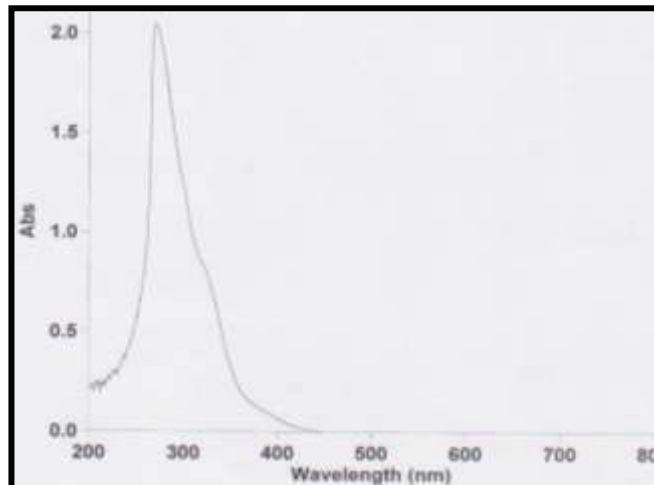


Figure (4): UV Spectrum of Na₂[Mn(Sac)₂(Ala)₂]

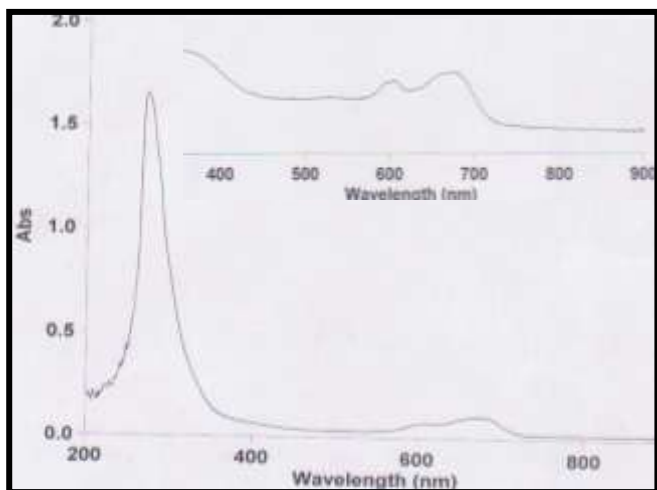


Figure (5): UV Spectrum of Na₂[Co(Sac)₂(Ala)₂]

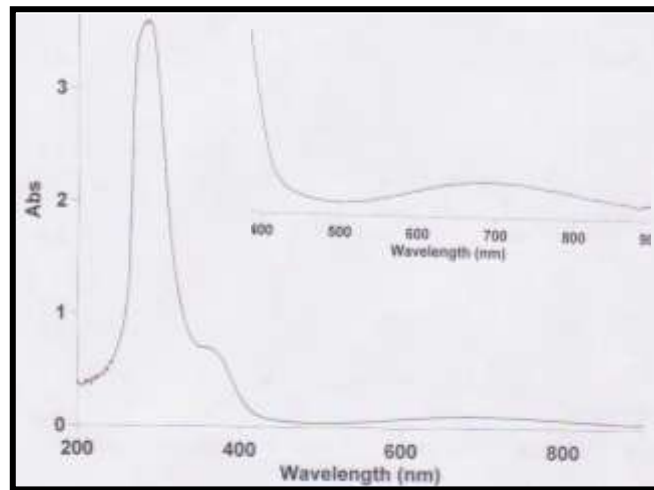


Figure (6): UV Spectrum of Na₂[Cu(Sac)₂(Ala)₂]

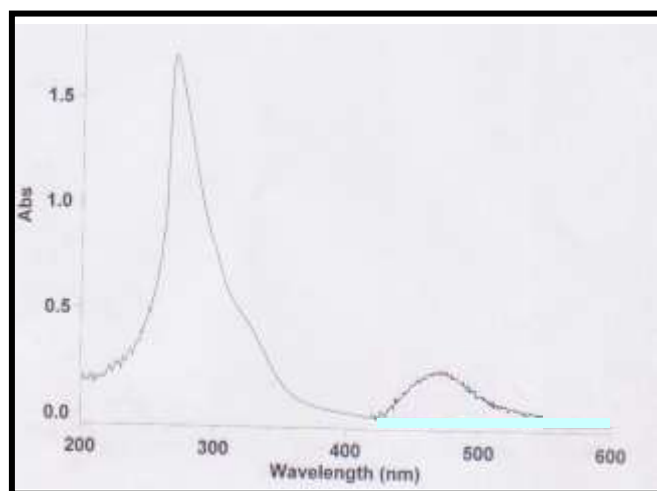


Figure (7): UV Spectrum of Na₂[Ni(Sac)₂(Ala)₂]

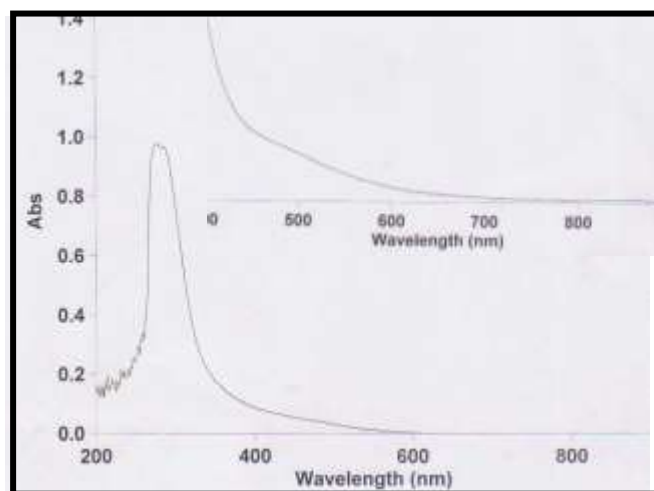


Figure (8): UV Spectrum of Na₂[Fe(Sac)₂(Ala)₂]

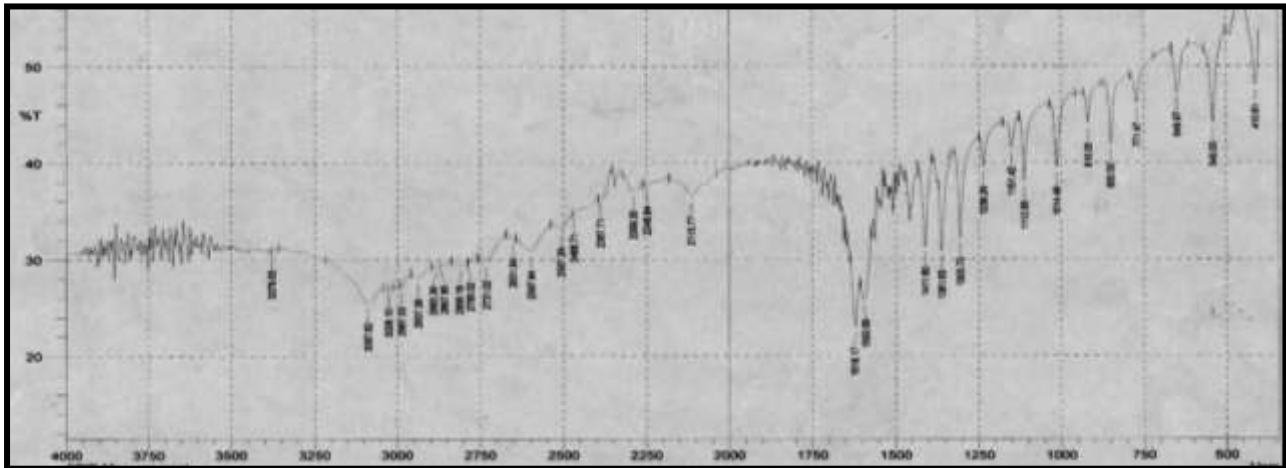


Figure (9): FT-IR of Alaninate ion

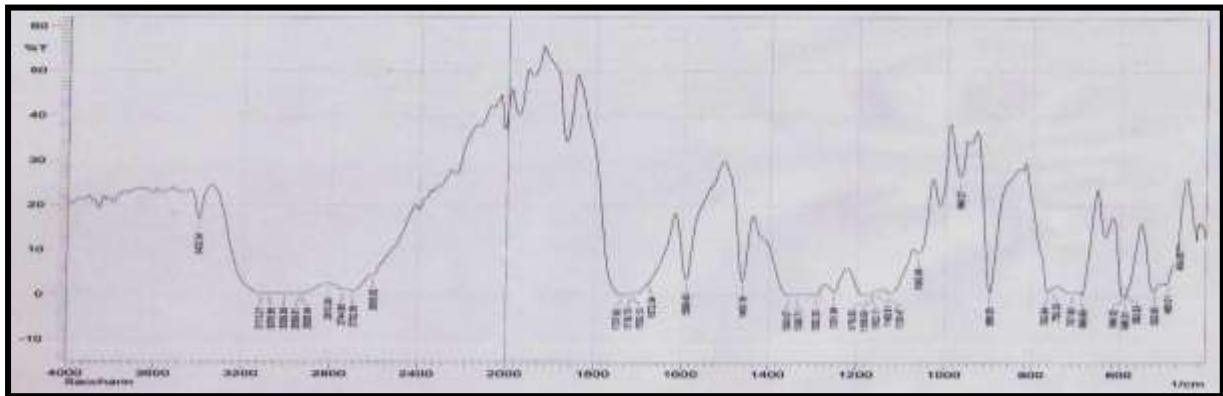


Figure (10): FT-IR spectrum of saccharine (C₇H₅NO₃S)

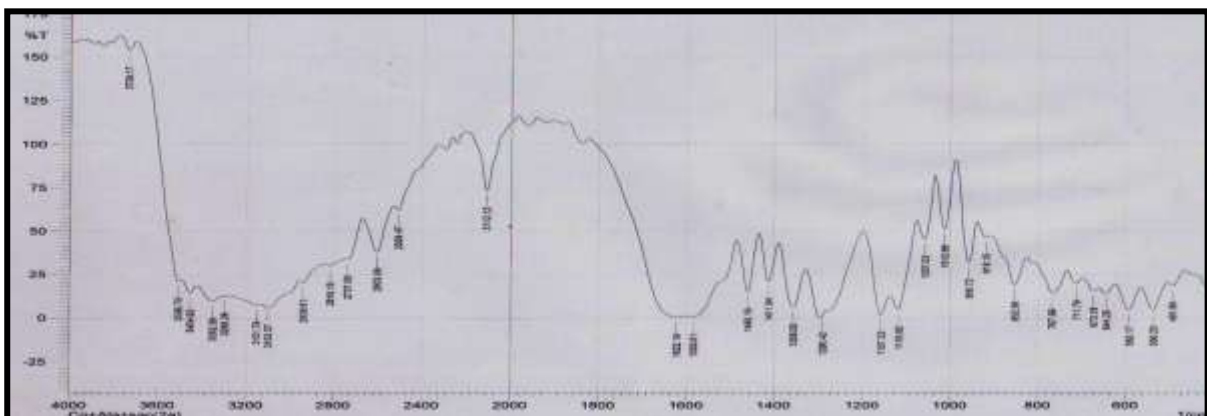


Figure (11): IR spectrum of Na₂[Co(Sac)₂(Ala)₂]

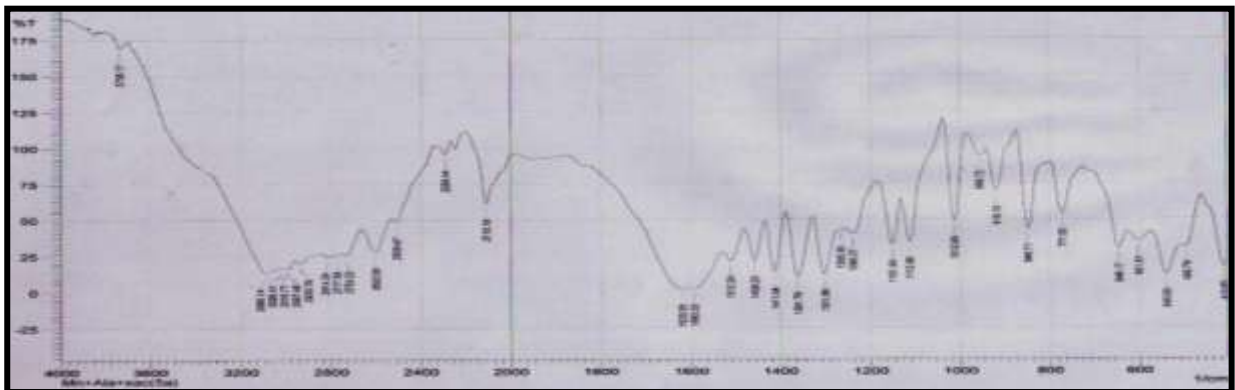


Figure (12): IR spectrum of $\text{Na}_2[\text{Mn}(\text{Sac})_2(\text{Ala})_2]$

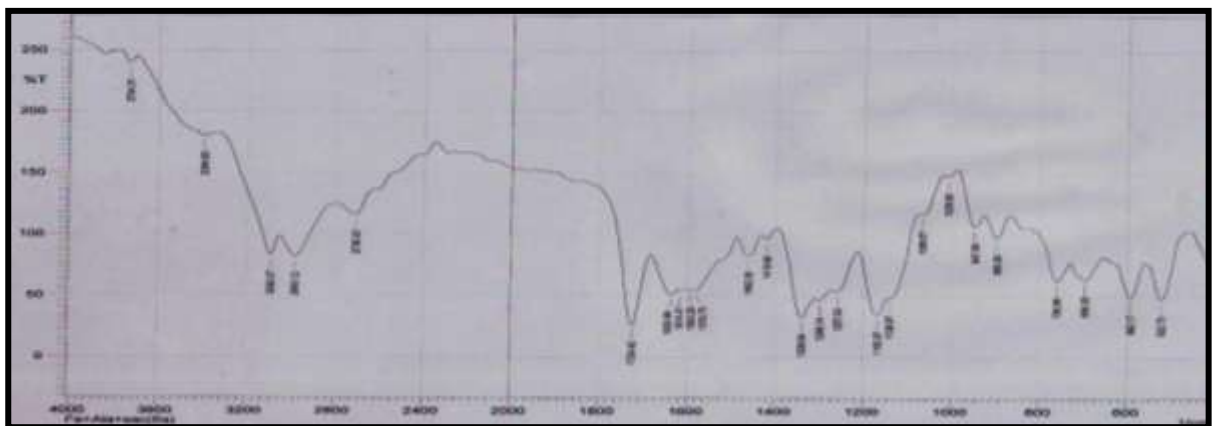


Figure (13): IR spectrum of $\text{Na}_2[\text{Fe}(\text{Sac})_2(\text{Ala})_2]$

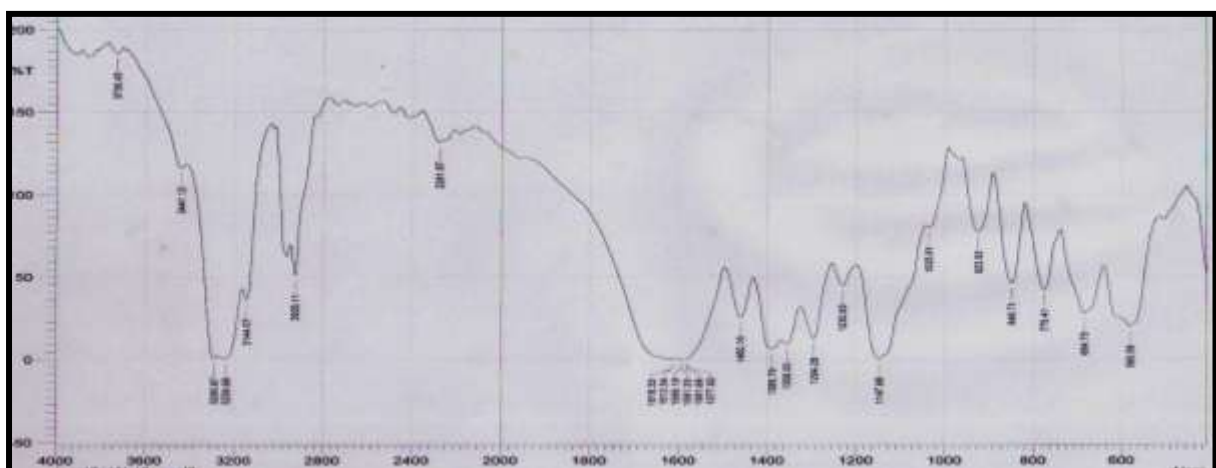


Figure (14): IR spectrum of $\text{Na}_2[\text{Cu}(\text{Sac})_2(\text{Ala})_2]$

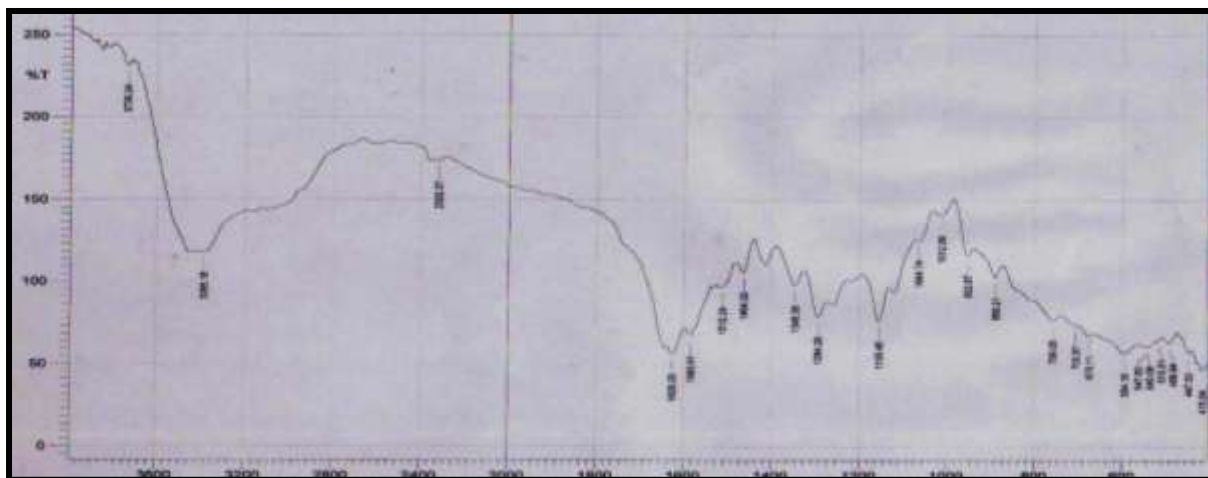


Figure (15): IR spectrum of $\text{Na}_2[\text{Ni}(\text{Sac})_2(\text{Ala})_2]$

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