

Synthesis and study of the mixed ligand (phenylalanine and anthranilic acid) with some transition Ions .

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الخلاصة :

تضمن هذا البحث تحضير وتشخيص معقدات ذات لكاندات مختلطة من حامض الانثرانيليك (A) وحامض الفينيل الأنين (phe) مع بعض أيونات العناصر الانتقالية .
تم دراسة المعقدات بالطرائق الآتية :
الدراسات الطيفية (UV-Vis , FT-IR) بالإضافة الى قياس درجات الانصهار والتفكك ، الذوبانية ، التوصيلية الكهربائية والتحليل الدقيق للعناصر ، الشكل المتوقع للمعقدات باستخدام برنامج (chem .office 3D(2000) .
ومن هذه المعطيات أمكن إعطاء الصيغة العامة الآتية للمعقدات المحضرة :



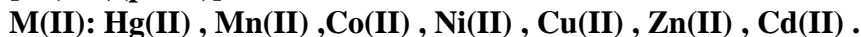
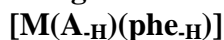
Abstract:

This paper presents the synthesis and study of some new mixed-ligand complexes containing anthranilic acid and amino acid phenylalanine (phe) with some metals .

The resulting products were found to be solid crystalline complexes which have been characterized by using (FT-IR,UV-Vis) spectra , melting point, elemental analysis (C.H.N) , molar conductivity .

The proposed structure of the complexes using program , chem office 3D(2000) .

The general formula have been given for the prepared complexes :



Introduction :

Anthranilic acid is known to specific precursor of the alkaloids skimmianine and acordine . (1)

There have been many reports on the metal-anthranilate complexes along with the structure of many of these compounds . Some transition metal anthranilates have capability for hydrogenation . (2,3) .

The new n-substituted anthranilic acid derivatives as potent anti inflammatory agents , the structure of these compounds have been established by IR, ¹H-NMR . Spectroscopic data and elemental analysis . (4)

During the recent years , there has been significant interest in the coordination chemistry , the structural properties and the reactivity of metal complexes of amino acids . (5-9) . Several amino acids nucleophilic side chains that coordinate to transition-metal ions . these ions may be intrinsic parts of the proteins and may be required the protein's structure or function . (10-13) .

We report here the preparation structural analysis of the M(II) complexes of mixed ligands (Anthranilic and phenylalanine) .

Experimental

A: Reagents and instruments : Anthranilic acid and phenylalanine were purchased from BDH .

All solutions and metal chloride were purchased from Merck and Fluka .

Electrical conductivity measurements of complexes were recorded at 25⁰C for 10⁻³ M solution of the sample in DMF using a PW (9526) digital conductivity .

Elemental (C.H.N) analyses were performed on (C.H. N) analyser model 1106 (Carlo-Erba) . Melting point were recorded by using Stuart melting point apparatus .

The FT-IR spectra were recorded using pressed KBr pellets with Fourier transform infrared spectrophotometer Shimadzu FT-IR-8300 .

The proposed molecular structure of the complexes were determined by using ChemOffice 2000, 3DX prog .

B: General synthesis :

Potassium anthranilate (K⁺Anth⁻) and potassium phenylalaninate (K⁺ phe⁻) prepared by neutralization of Anthranilic acid (AnthH) [1mmol] and phenylalanine (pheH) [1mmol] with 1mmol potassium hydroxide in water at 20⁰C respectively .

The complexes were prepared by addition (K⁺Anth⁻) and (K⁺phe⁻) to warm stirred aqueous solution of the respective metal (II) chloride in the stoichiometric ratio after cooling of the solution pale pink well-shaped crystals of the cobalt compound , light green crystals of the nickel compounds and colorless crystals of the Zn(II) , Cd(II) and Hg(II) were obtained . The compounds are soluble in water , the crystals were filtered , washed with acetone and dried at room temperature . (14) .

Results and Discussion :

Physical properties and elemental analysis are presented in Table (1) . Formula $M(\text{Anth}_H)(\text{phe}_H)$ giving good agreement between the observed and the calculated values by elemental analysis . All complexes dissolved in DMF solvent . The molar conductance values of the complexes in DMF solvent in 10^{-3}M at 298^0K indicated Non-electrolyte . (15)

The electronic spectra :

The electronic spectra of all compounds (Ligands and complexes) are listed in Table (2) . The spectrum of the free ligand (phe_H) in DMF solvent show a high intensity band in wave length 271.5nm (36832.42 cm^{-1}) ϵ_{max} ($1574\text{ l.mol}^{-1}.\text{cm}^{-1}$) assigned to ($n \rightarrow \pi^*$) . (16) and free ligand (A_H) show a high intensity band in wave length in 271nm (36832 cm^{-1}) ϵ_{max} ($1574\text{ l.mol}^{-1}.\text{cm}^{-1}$) .

In the $[\text{Ni}(\text{phe}_H)(\text{A}_H)]$ complexes the two bands at (482 and 332) nm are attributed to ($d-d$) electronic transition [${}^3\text{A}_2(\text{f}) \rightarrow {}^3\text{T}_1(\text{f})$] and [${}^3\text{A}_2(\text{f}) \rightarrow {}^3\text{T}_2(\text{f})$] respectively suggesting a square planer geometry about Nickel atom . (17) .

In the $[\text{Cu}(\text{phe}_H)(\text{A}_H)]$ complex the two bands at (581 and 357) nm are assigned to [${}^2\text{B}_1 \rightarrow {}^2\text{A}_1$] and [${}^2\text{B}_1 \rightarrow {}^2\text{E}$] transitions in a distorted square planer geometry . (14) .

Fourier-transform infrared spectra :

The assignment of some of the most characteristic FT-IR band of the complexes are shown in Table (3) together with those of sodium phenylalaninate and sodium anthranilate recorded for comparative purposes and facilitate the spectral analysis .

Absorption bands in the ($509-570$) cm^{-1} region are considered to be due to metal-nitrogen vibrations [18,19] whilst those occurring around ($460-510$) cm^{-1} are thought to arise from metal-oxygen vibration . (20,21) the sharp bands at ($3325-330$) cm^{-1} are attributed to the N-H stretching . (22) .

Nomenclature of prepared complexes :

Table (4) shows empirical formula and nomenclature (IUPAC) with abbreviated .

Table (4) Nomenclature of prepared complexes

Complexes	Nomenclature	Abbreviation
$\text{Mn}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	AnthranilatophenylalaninatoManganese (II)	$\text{Mn}(\text{A}_H)(\text{phe}_H)$
$\text{Co}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	AnthranilatophenylalaninatoCobalt (II)	$\text{Co}(\text{A}_H)(\text{phe}_H)$
$\text{Ni}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	AnthranilatophenylalaninatoNickel(II)	$\text{Ni}(\text{A}_H)(\text{phe}_H)$
$\text{Cu}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	AnthranilatophenylalaninatoCopper (II)	$\text{Cu}(\text{A}_H)(\text{phe}_H)$
$\text{Zn}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	AnthranilatophenylalaninatoZinc (II)	$\text{Zn}(\text{A}_H)(\text{phe}_H)$
$\text{Cd}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	AnthranilatophenylalaninatoCadmium (II)	$\text{Cd}(\text{A}_H)(\text{phe}_H)$
$\text{Hg}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	AnthranilatophenylalaninatoMercury (II)	$\text{Hg}(\text{A}_H)(\text{phe}_H)$

Proposed molecular structure :

Studying complexes on bases of the above analysis , the existence of tetracoordinated $[\text{M}(\text{phe}_H)(\text{A}_H)]$, $\text{M}(\text{II}) =$

A proposed models of the speciese were built with chem 3D (23) shows in Fig (1) .

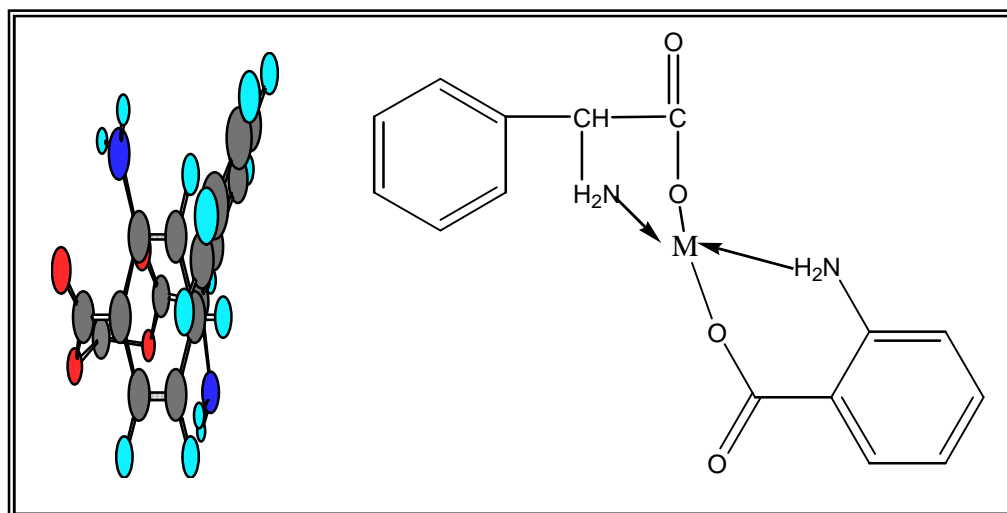


Fig (1) : The proposed structure of the complexes

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Table (1) The physical properties of the complexes

Compound	Colour	M.P.C°	Dec°	Elemental Analysis						Molar conductivity Assem. cm ² Mol ⁻¹ 10 ⁻³ M in DMF
				%C		%H		%N		
				Calc.	Found	Calc.	Found	Calc.	Found	
C ₇ H ₇ NO ₂	White	137	-	-	-	-	-	-	-	9.6
C ₉ H ₁₁ NO ₂	White	272	-	-	-	-	-	-	-	2.8
Mn(C ₁₆ H ₁₆ N ₂ O ₄)	Pale-yellow	-	225	54.09	54.66	4.54	4.56	7.89	7.85	3.67
Co(C ₁₆ H ₁₆ N ₂ O ₄)	pink	-	>350	53.49	53.99	4.49	4.58	7.80	7.90	3.95
Ni(C ₁₆ H ₁₆ N ₂ O ₄)	Light-green	-	>250	53.53	53.90	4.49	4.96	7.80	7.90	3.55
Cu(C ₁₆ H ₁₆ N ₂ O ₄)	Dark-green	-	235	52.81	52.99	4.43	4.88	7.70	7.90	5.26
Zn(C ₁₆ H ₁₆ N ₂ O ₄)	White	-	205	52.55	52.65	4.41	4.70	7.66	7.56	2.80
Cd(C ₁₆ H ₁₆ N ₂ O ₄)	White	-	>350	46.56	46.80	3.91	4.01	6.79	6.70	2.15
Hg(C ₁₆ H ₁₆ N ₂ O ₄)	White	-	>350	38.37	38.39	3.22	3.20	5.59	5.61	1.55

M.P = melting point
Dec. = Decomposition temperature

Table (2) : Electronic Spectra of the studied complexes and two ligands

Compounds	$\lambda(\text{nm})$	$\nu(\text{cm}^{-1})$ wave number	$\epsilon_{\text{max}} (\text{l.mol}^{-1} \text{cm}^{-1})$	Assignment of the transition
$\text{C}_7\text{H}_7\text{NO}_2$	271	36832	1574	$\pi \rightarrow \pi^*$
$\text{C}_9\text{H}_9\text{NO}_2$	271.5	36832.42	1754	$\pi \rightarrow \pi^*$
$\text{Mn}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	482	20661	19	Ligand Field
	326	30674.8	1619	${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_1$
$\text{Co}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	424	23584.9	198	${}^4\text{A}_{2g} \rightarrow {}^2\text{T}_1$
	330	30303	1531	Ligand Field
$\text{Ni}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	482	20746.8	12	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$
	332	30120.4	362	
$\text{Cu}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	581	17211.7	37	${}^2\text{B}_1 \rightarrow {}^2\text{A}_1$
	357	28011.2	1018	${}^2\text{B}_1 \rightarrow {}^2\text{E}$
$\text{Zn}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	514	19455	13	Charge transfer
	332	30120	1528	Ligand Field
$\text{Cd}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	825	12121	20	Charge transfer
	323	30959.7	1584	Ligand Field
$\text{Hg}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	617	16707	186	Charge transfer
	323	30959.7	1866	Ligand Field

CT : charge transfer

Table (3) : FT-IR spectral data of the Ligands and its complexes:

Compound	$\nu(\text{NH}_2)$	$\nu(\text{N-H})$	$\nu\left(\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}^- \end{array}\right)_{\text{asy}}$	$\nu\left(\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}^- \end{array}\right)_{\text{sy}}$	$\Delta\left(\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}^- \end{array}\right)_{\text{asy-sy}}$	M-N	M-O
$\text{C}_2\text{H}_7\text{NO}_2$	3380 s	3330 vs	1650 s	1400 s	-	-	-
$\text{C}_6\text{H}_{11}\text{NO}_2$	3410 m	3350 s	1560 vs	1420 ms	140	-	-
$\text{Mn}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	3436 mb	3326 ws 3370ms	1595 ms	1230 vs	365	560	490
$\text{Co}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	3960 b	3340 ms 3370 m	1610 ms	1253 ms	370	570	510 w
$\text{Cu}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	4366 ms	3255 mb 3366 ws	1598 m	1280	318	518	492 m
$\text{Ni}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	4376 ms	3355 ws 3366 ws	1620 sb	1290 m	330	526	495 m
$\text{Zn}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	3306 m	3325 vs	1600sh	1280	320	536	460
$\text{Cd}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	3355 m	3325 vs	1620	1282	345	522	460
$\text{Hg}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4)$	3420 vs	3370 ws	1620 ms	1275 vs	345	509	472

asy = asymmetry

sy = symmetry

s = sharp

vs = very sharp

w = weak

ms = middle sharp

mb = middle broad