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

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Abstract

This paper presents the synthesis and study of some new mixed-liagnd complexes containing tow amino acids[Alanine(Ala) and phenylalanine (phe)] with some metals .

The results 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 and solubilty
The proposed structure of the complexes using program , chem office 3D(2000) .
The general formula have been given for the prepared complexes :
[M(A-H)(phe-H)]
M(II): Hg , Mn ,Co , Ni , Cu) , Zn , Cd(II) .
Ala = Alanine acid = $C_3H_7NO_2$
Phe = phenylalanine = $C_9H_{11}NO_2$

الخلاصة

تضمن هذا البحث تحضير وتشخيص معقدات مزيج الكاندات من الحامض الالانين وحامض الفنيل ألانين مع بعض أيونات العناصر الانتقالية و تم دراسة المعقدات بالطرائق الطيفية الآتيـــة : (FT-IR,UV-Vis) بالاضافة الى قياس درجات الانصهار والتفكك ، الذوبانية ، التوصيلية الكهربائية والتحليـــل الــــدقيق للعناصر ، الشكل المتوقع للمعقدات باستخدام برنامج chem .office 3D(1997) .

ومن هذه المعطيات أمكن إعطاء الصيغة العامة الآتية للمعقدات المحضرة :

M(Ala-H)(phe-H)
M(II): Hg , Mn ,Co , Ni , Cu , Zn and Cd .
Ala = Alanine acid = $C_3H_7NO_2$
Phe = phenylalanine = $C_9H_{11}NO_2$

Introduction

Numerous papers have been published on metal complexation of amino acids and derivatives during the past ten years. Different spectroscopic, calorimetric, electrochemical and X-ray diffraction characterize the complexes methods were used, and in many cases several methods were combined to Prepared(1,2,3). The main interest in transition metal complexes has remained, but the number of results for complexes of other complexes of amino acids/derivatives have recently have been discovered. Besides some new platinum(II) and palladium(II) complexes, (4,5,6,7) some organotin,(8) lanthanide(9) gold,(10)and copper(11-13) complexes were also found to be biologically active

In this paper we describe the synthesis and characterization of the amino acids (Alanine and phenylalanine)and their coordination complexes with different metal ions.

Experimental

Reagents were purchased from fluka & Redial-Dehengc CO.I.R spectra were recorded as KB discs using perkin-Elmer 1330 Infrared Spectrophotometer and Fourier Transform Infrared Spectrophotometer Shimadzu 24FT-I.R8300. 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 Visib-Spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. Elemental microanalysis (C.H.N) were performed by using perk in – Elmer 24B Elemental Analysis . While metal contents of the complexes were determined by Atomic Absorption (A.A)Technique using Japan A.A-670 Shimadzu. Electrical conductivity measurements of the complexes were recorded at 25?C for 10^{-3} M solutions of the samples in DMF using pw9527 digital conductivity meter (Philips).

Melting points were recorded by using Stuart melting point apparatus

The proposed molecular structure of the complexes were determinate by using chem. office - 3DX prog (1997).

General synthesis(14)

prepared by naturalization of Alanine acide (Ala) [1mmol ,0.089g] and phenylalanine (phe) [1mmol ,0.165g] with 1mmol potassium hydroxide in water at 200C respectively .mixed ligand complexes were prepared as follows |(L-Alaninato)
(L-phanylalaninito)
[metal(II)=Mn ,Co ,Ni ,Cu ,Zn ,Cd), and Hg].

The complexes were prepared by mixing equimoler (1mmol)aqueous solution of (K^+Ala^-) and (K^+phe^-)were added simultaneously to another aqueous solution containing (1mmol)of the respective metal (II) chloride (MCl_2)in the stoichiometric ratio(14).All the The complexes which precipitated almost immediately were suction- filtered, washed with 50%(v/v)aqueous ethanolic solution ,dried at room temperature and analyzed employing standard method .

Results and Discussion

Physical properties and elemental analysis are presented in Table (1) . Formula M(Ala$_{-H}$) (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 K indicated non-electrolyte (15) .

The electronic spectra :

The electronic spectra of all compounds (Ligands and complexes) are listed in table (2) together with the proposed assignments and suggested geometry. The spectrum of the free ligand (phe-H) in DMF solvent show a high intensity band in wavelength

271.5nm (36832.42 cm^{-1}) εmax (1574 $l.mol^{-1}.cm^{-1}$) assigned to (n→π*) (16) and the spectrum of the free ligand (Ala_{-H})in same solvent show two high intensity band in wavelength 304nm (32894 cm^{-1}) εmax (391$l.mol^{-1}.cm^{-1}$) and277nm. (36101 cm^{-1}) εmax (343$l.mol^{-1}.cm^{-1}$) assigned to(n→ π *)and (π → π*)transition respectively (17).

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 phanylalalinate and sodium alaninate(Figs 2and 3)recorded for comparative purposes and facilitate the spectral analysis .

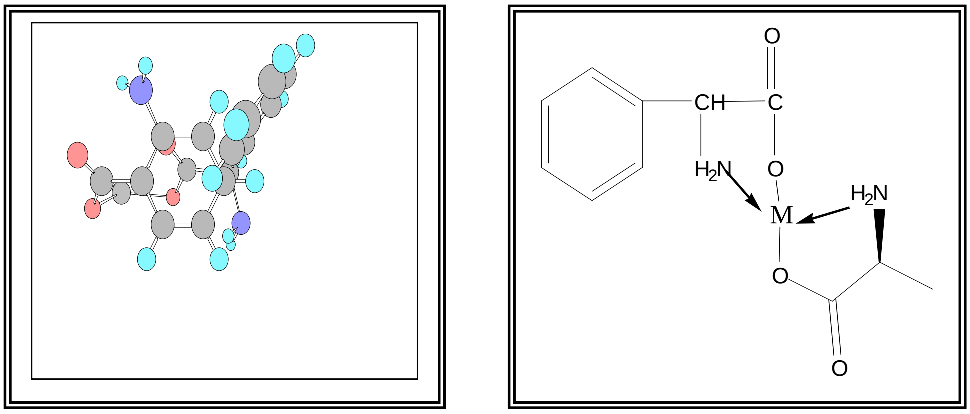
Absorption bands in the (446-584)cm^{-1} region are considered to be due to metal-nitrogen vibrations (18-19) whilst those occurring around (430-460)cm^{-1} are thought to arise from metal-oxygen vibration . (20,21) the sharp bands at (3378-3335) cm^{-1} are attributed to the N-H_2stretching . (22) .The IR spectra show strong evidence in support of involvement of carboxylate group in coordination. In comparison with free amino acids .

Nomenclature of prepared complexes :

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

Proposed molecular structure :

Studying complexes on bases of the above analysis , the existence of tetracoordinated [M(phe_{-H})(Ala_{-H})] , M (II)=Mn,Co ,Ni ,Cu ,Zn ,Cd , and Hg . The tow ligands coordinated to the metal ion as uninagative bidentate Ligands through the oxygen atom in the carboxyl group (COO^-) and the nitrogen atom of the (-NH_2) ,A proposed models of the speciese were built with chem 3D (23) shows in Fig (1) . as shown below .



(a) Crystal (b)Empirical Structural

Fig (1) : The proposed structure of the complexes

Table (1) the physical properities of the complexes

Compound	Colour	M.P.C°	%C		%H		%N		Molar conductivity ΛSem .cm^2. Mol^{-1} 10^{-3}M in DMF
			Calc.	Found	Calc.	Found	Calc.	Found	
$C_3H_7NO_2$	White	272							1.3
$C_9H_{11}NO_2$	White	291							7.26
$[Mn(C_{12}H_{16}N_2O_4)]$	Dark brown	>350d	46.91	45.28	5.25	5.60	9.11	9.80	12.78
$[Co(C_{12}H_{16}N_2O_4)]$	Pale-brown	>350d	46.32	47.12	5.18	5.98	8.99	9.12	15.78
$[Ni(C_{12}H_{16}N_2O_4)]$	Pale-blue	>350d	46.36	45.33	5.19	5.40	9.01	8.95	3.53
$[Cu(C_{12}H_{16}N_2O_4)]$	Dark-blue	239d	45.65	44.20	5.11	5.36	8.87	8.80	6.78
$[Zn(C_{12}H_{16}N_2O_4)]$	White	280d	45.38	43.38	5.08	5.28	8.82	8.80	12.88
$[Cd(C_{12}H_{16}N_2O_4)]$	White	>350d	39.53	40.7	4.42	4.96	7.68	8.06	15.48
$[Hg(C_{12}H_{16}N_2O_4)]$	Brown	263d	31.83	32.95	3.56	4.03	6.18	7.01	4.31

d =decomposition temp.

Table (2) electronic spectra of the studied complexes and two ligands

Compounds	λ(nm)	υ(cm^{-1}) wave number	ε_{Max} (l.mol^{-1}.cm^{-1})	Assignment of the transition
$C_3H_7NO_2$	276 304	36101 32894	343 391	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
$C_9H_{11}NO_2$	271.5	36832	157	$n \rightarrow \pi^*$
$Mn(C_{12}H_{16}N_2O_4)$	217 344	46296 2918	362 158	Ligand Field $^4T_{1(p)} \rightarrow {}^4A_1$
$Co(C_{12}H_{16}N_2O_4)$	554 383 272	18050 261096 36764	234 635	$^4A_{2(F)} \rightarrow {}^4T_1$ Ligand Field
$Ni(C_{12}H_{16}N_2O_4)$	614 415	16286 24690	186 234	$^3A_{2(f)} \rightarrow {}^3T_{1(f)}$ $^3A_{2(f)} \rightarrow {}^3T_{1(p)}$
$Cu(C_{12}H_{16}N_2O_4)$	639 448 271	15649 22321 36900	207 181 572	$^2B_1 \rightarrow {}^2A_1$ $^2B_1 \rightarrow {}^2E$ Ligand field
$Zn(C_{12}H_{16}N_2O_4)$	267 432	3743 23148	184 158	Charge transfer Ligand Field
$Cd(C_{12}H_{16}N_2O_4)$	260 415	38461 24096	129 251	Charge transfer Ligand Field
$Hg(C_{12}H_{16}N_2O_4)$	298	33557	986	Ligand Field

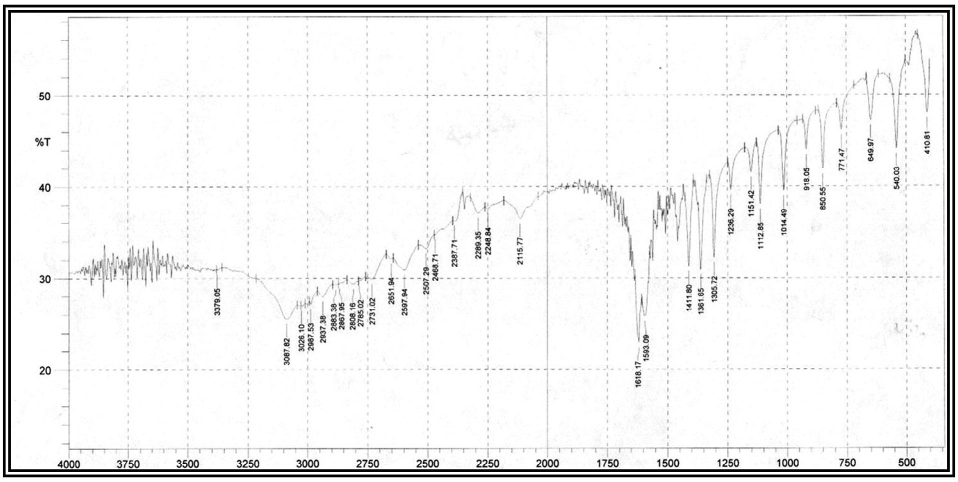
Table (3) IR important band at cm^{-1} (KBr or CsI disc)

Compound	$\upsilon(NH_2)$	$\upsilon(N-H)$	$\upsilon(-\overset{O}{\overset{\|}{C}}-O^-)_{asy}$	$(-\overset{O}{\overset{\|}{C}}-O^-)_{sy}$	M–N	M–O
$C_3H_7NO_2$	3379m	3087m	1618s	1411s		
$C_9H_{11}NO_2$	3410 m	3350 s	1560 s	1420 ms	-	-
$Mn(C_{12}H_{16}N_2O_4)$	3488m	3377s	1436s	1394m	53 6 m	436w
$Co(C_{12}H_{16}N_2O_4)$	3456s	3356m	1456s	1335m	533vm	456m
$Cu(C_{12}H_{16}N_2O_4)$	3458s	3352s	1499s	1356vw	518m	451m
$Ni(C_{12}H_{16}N_2O_4)$	3447m	3356s	1489w	1338w	555m	455m
$Zn(C_{12}H_{16}N_2O_4)$	3345m	3354s	1477m	1384m	525m	469m
$Cd(C_{12}H_{16}N_2O_4)$	3456s	3387m	1489w	1358w	574m	459m
$Hg(C_{12}H_{16}N_2O_4)$	3345s	3344s	1475m	1337w	449m	420m

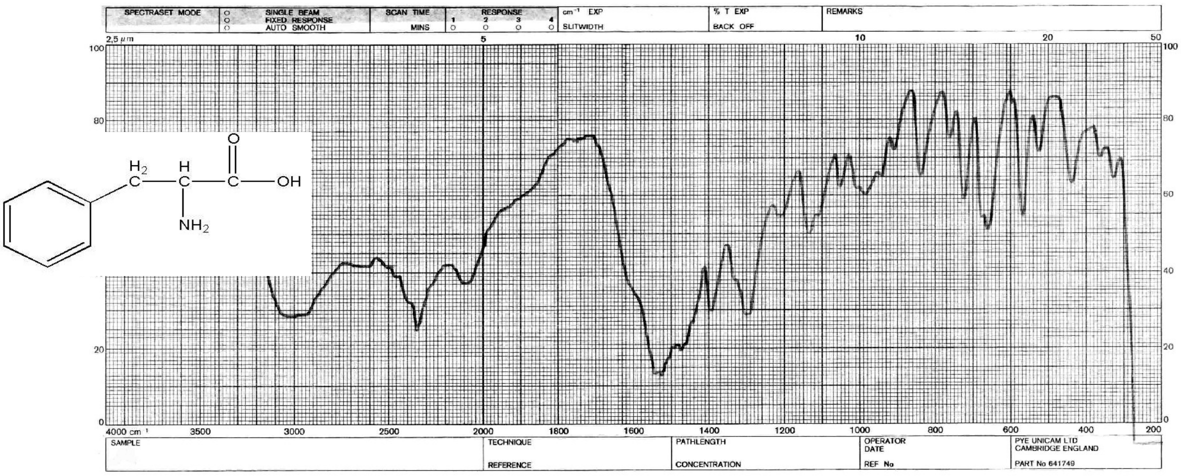
Asy= asymetry sy= symmetry s= sharp w= week ms =middle sharp mb= middlebroad

Table (4) IUPC name of prepared complexes

Complexes	IUPC name	Abbreviation
$Mn(C_{12}H_{16}N_2O_4)$	AlaninatophenylalaninatoManganese (II)	$Mn(Ala_{-H})(phe_{-H})$
$Co(C_{12}H_{16}N_2O_4)$	AlaninatophenylalaninatoCobalt (II)	$Co(Ala_{-H})(phe_{-H})$
$Ni(C_{12}H_{16}N_2O_4)$	AlaninatophenylalaninatoNickel(II)	$Ni(Ala_{-H})(phe_{-H})$
$Cu(C_{12}H_{16}N_2O_4)$	AlaninatophenylalaninatoCopper (II)	$Cu(Ala_{-H})(phe_{-H})$
$Zn(C_{12}H_{16}N_2O_4)$	AlaninatophenylalaninatoZinc (II)	$Zn(Ala_{-H})(phe_{-H})$
$Cd(C_{12}H_{16}N_2O_4)$	AlaninatophenylalaninatoCadmium (II)	$Cd(Ala_{-H})(phe_{-H})$
$Hg(C12H_{16}N_2O_4)$	AlaninatophenylalaninatoMercury (II)	$Hg(Ala_{-H})(phe_{-H})$



Fig(2) FT-IR Alaninate ion



Fig(3) FT-IR Phanyl alaninato

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