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Metal Chelates of the Amino Acid Schiff Bases: Preparation and `Spectroscopic Investigation

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Abstract Schiff base chelates of V(IV), Ni(II) and Cu(II) ions derived from 4-dimethylaminobenzaldehyde with valine (L1) and with tyrosine (L2) were prepared and investigated by using some physical tools, in terms, elemental analyses, molar conductance measurements, thermogravimetric analysis, magnetic moments, infrared, electronic and electron paramagnetic resonance spectroscopies. The CHN elemental analyses showed the formation of 1:1 and 1:2 [M:L] ratios. The molar conductivity measurements revealed that the chelates are non electrolyte in nature. The magnetic moment results showed a paramagnetic phenomenon for all chelates. The infrared spectral data displayed the proper coordination sites of the Schiff bases toward the metal ions. The electronic absorption spectral results showed the proper electronic transitions and the expected chemical structures for the chelates. The electron paramagnetic resonance spectral data exhibited an octahedral geometry structure for V(IV) Ni(II) and Cu(II) chelates with L^1 and L^2, while a square planar for Cu(II)L^2 chelate.
Key words: 4-dimethylaminobenzaldehyde, L-Valine, L-tyrosine, Schiff bases, Metal chelates.

متراكبات مخلبية للفلزات مع قواعد شف من احماض أمينية، تحضير وتشخيص طيفي

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الملخص تم تحضير وتشخيص متراكبات قواعد شف لأيونات الفانديوم(IV) والنيكل(II) والنحاس(II) والمشتقة من 4،4–ثنائى ميثيل امينوبنزالدهيد مع الفالين والتيروسين وتم التشخيص باستخدام عدة طرق فيزيائية منها التحليل العنصرى للكربون والهيدروجين والنيتروجين (CHN) والقياسات المولارية الجهدية والقياسات المغناطيسية ومطيافية الأشعة تحت الحمراء والمطيافية الإلكترونية ومطيافية الرنين الإلكترونى البارامغناطيسي . وقد بينت نتائج التحليل العنصرى أن المتراكبات تكونت بنسب 1:1 و 1:2 (فلز: ليجاند) . كما أظهرت نتائج القياس المولارى للمتراكبات بإنها غير إلكتروليتية فى طبيعتها . اما القياسات المغناطيسية تؤكد بان جميع المتراكبات التي تم تحضيرها بارامغناطيسية . هذا وبينت مطيافية الاشعة تحت الحمراء مواقع التناسق الموجودة بمركبات قواعد شف تجاه أيونات الفلزات. وأوضحت نتائج مطيافية الأشعة الإلكترونية الانتقالات الإلكترونية المحتملة والتراكيب الكيميائية للمتراكبات . اما مطيافية الرنين الإلكترونى البارامغناطيسى أكدت وجود تركيب ثمانى الاسطح الهرمية لمتراكبات الفانديوم(IV) والنيكل(II) مع L^1 و L^2 ، اما النحاس(II) فهو ثمانى الاسطح الهرمية مع L^1 ومربع مسطح مع L^2.
الكلمات الافتتاحية: 4–ثنائى ميثيل امينوبنزالدهيد، الفالين، التيروسين، قواعد شف، متراكبات مخلبية.

Introduction

The interest in the synthesis and characterization of Schiff base complexes has been prompted [1, 2] by the belief that the systematic characterization of these complexes may shed light on the nature of the free ligand environment. El-ajaily et al [3] Prepared and investigated the Ni(II) chelate of a Schiff base derived from 4-dimethylaminobenzaldehyede and cysteine. Based on the physiochemical tools, a square planar structure was proposed for the chelate. The Schiff base complexes derived from the condensing 4-[N,N-dimethylamino]benzaldehyde and o-aminophenol have been prepared and investigated by several physical techniques. The obtained data showed the formulae of $[NiL(OH)(H_2O)].5H_2O$ and $[ML(OH)(H_2O)].4H_2O$ complexes in which M represents Cr(III) or Fe(III) ion. The analysis data suggested a square planar geometry for Ni(II) complex and octahedral structures for Cr(III) and Fe(III) complexes [4]. Vaghasiya et.al [5] synthesize and determine the geometrical structures of the compounds derived from vanillin and 4-aminoantipyrine. Also the antibacterial activity of the synthesized compound were screened on some pathogenic bacteria.This study aims to synthesis and elucidate the geometrical structures of some

metal chelates of VO(IV), Ni(II) and Cu(II) ions with Schiff bases derived from 4-dimethylaminobenzaldehyde, valine and tyrosine.

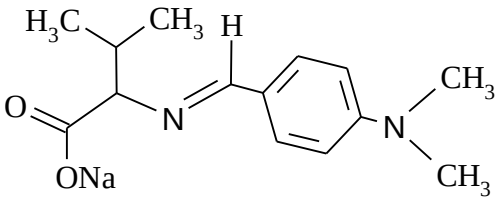
Experimental

Chemicals and methods

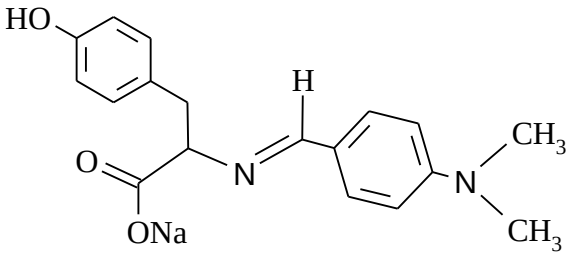
All chemicals used in this investigation were laboratory pure (BDH or Aldrich) including 4-dimethylaminobenzaldehyde, valine, tyrosine, $VOSO_4.3H_2O$, $NiCl_2.6H_2O$, $Cu(CH_3COO)_2.H_2O$, NaOH, C_2H_5OH, CH_3OH, $CHCl_3$, DMSO, acetic acid and double distilled water. The prepared Schiff base complexes were subjected to (CHN) 2400-elemental analyzer. The molar conductance measurements were carried out in DMSO solvent using conductivity meter model CMD-650 digital, Chemistry department, Benghazi university. The magnetic moment measurements of the complexes were measured by using magnetic susceptibility balance Sherwood Scientific England. The Infrared spectra were obtained by using KBr disk technique on IFS-25-DPUS/Infrared spectrometer (Bruker) in the range of 4000-400cm^{-1}. The electronic absorption spectra of the complexes were measured in $CHCl_3$ solvent using UV-Vis-NIR-3101PC Schimadzu (Japan). The electron paramagnetic resonance spectra were recorded by using EMX ESR spectrometer (Bruker) 1998Y.

Preparation of valine Schiff base (L1)

The Schiff base derived from 4-dimethylaminobenzaldehyde and valine was prepared as follows: NaOH (10mmol; 0.4g) was dissolved in methanol (20cm^3) then L-valine (10mmol) was added. The mixture was stirred magnetically at room temperature. When the mixture became homogeneous, a solution of 4-dimethylaminobenzaldehyde (10mmol, 1.49g) in ethanol (20cm^3) was added. After 2minutes, the solution was evaporated to 20% of its original volume and 1 cm^3 of acetic acid was added immediately. After 2 hours yellow crystals appeared. The crystals were filtered and washed with ethanol and recrystallized from hot methanol to give yellow crystals of melting point 245°C and yielded 75.40%..



L^1



L^2

Preparation of tyrosine Schiff base (L2)

This compound which formed by the condensation of 4-dimethylamino- benzaldehyde and tyrosine was prepared as follows: NaOH (10mmol, 0.4g) was dissolved in methanol (20 cm^3) and then L-tyrosine] (10mmol) was added. The mixture was stirred until the mixture becomes homogeneous. A solution of 4-dimethylaminobenzaldehyde (10mmol; 1.49 g) in ethanol (20 cm^3) was added. After 2 minutes, the solution was evaporated to 20% of its original volume and 1cm^3 of acetic acid was added immediately. After 2 hrs yellow crystals appeared. The crystals were filtered and washed with ethanol. They were recrystallized from hot methanol to give yellow crystals of melting point of 250°C and yield of 84.70%.

Preparation of the valine Schiff base chelates

The valine (20 mmol; 4.96g) was dissolved in (25cm^3) of methanol containing NaOH (20mmol; 0.8g). A solution of 4-dimethylaminobenzaldehyde (20 mmol, 2.98g) in (25 cm^3) of ethanol was added to the solution. After 2minutes, Solutions of the metal salts [10mmol, $VOSO_4.3H_2O$ (2.01g), $NiCl_2.6H_2O$ (2.37g) and $Cu(CH_3COO)_2.H_2O$ (1.99g)] were added and the mixtures were refluxed for 3hrs. The solution volumes were reduced to 75% by evaporation and the residues were left to stand overnight, reddish brown microcrystalline solids were filtered and recrystallized from a methanol/ ethanol (50%) mixture.

Preparation of the tyrosine Schiff base chelates

The L-tyrosine (20mmol; 6.24g) was dissolved in (25 cm^3) of methanol containing NaOH (20mmol; 0.8g). An ethanolic solution of 4-dimethyl-aminobenzaldehyde (20mmol; 2.98g) in (25 cm^3) was added to the solution. After 2mins, solutions of the metal salts [10mmol, $VOSO_4.3H_2O$ (2.01g), $NiCl_2.6H_2O$ (2.37g) and $Cu(CH_3COO)_2.H_2O$ (1.99g)] were added and the mixtures were condensed for 3hrs. The obtained mixtures were reduced to 75% by evaporation and the residues were left to stand overnight, reddish brown microcrystalline solids were filtered and recrystallized from a methanol/ ethanol (50%) mixture.

Results and discussion

Microanalysis and molar conductance measurements

The elemental analysis data of the Schiff base chelates (Table-1) show the formation of 1:1 [M:L] and 1:2 [M:L] ratios. It is found that the theoretical values are in a good agreement with the found ones. The purity of the Schiff base chelates were tested by TLC technique and CHN elemental analyses. The molar conductance measurements of the chelates were carried out in DMSO solvent and the obtained values (Table-1)

were taken as a good evidence for the existence of a non-electrolyte nature for all chelates [6].

Table-1: CHN elemental analyses and some properties of Schiff base chelates

Schiff base/Chelates	M.Wt	Yield (%)	C% Calc.	C% Exp.	%H Calc.	%H Exp.	%N Calc.	%N Exp.	μ BM	Λ*
Valine Schiff base (L^1)	301	5.41	51.85	50.53	800	9.25	8.64	9.78	-	-
Tyrosine Schiff base (L^2)	365	84.7	56.99	57.08	6.33	6.53	7.38	7.25	-	-
$[VOL^1(OH)(H_2O)_2]$	443.	60.0	38.00	.39.4	6.56	5.84	6.33	5.64	1.27	0.00
$[NiL^1(OH)(H_2O)_2].7H_2O$	560.7	62.6	29.98	30.35	7.66	6.57	4.99	5.29.	2.08	5.90
$[CuL^1(OH)(H_2O)_3].7H_2O$	582.5	70.0	28.84	29.56	6.52	5.88	4.81	5.19	1.28	38.00
$[VO(L^2)_2(H_2O)].H_2O$	787	55.8	56.00	56.17	5.96	5.20	7.56	7.28	1.63	0.00
$[NiL^2(OH)(H_2O)_3].10H_2O$	687.7	60.3	31.41	30.84	5.38	5.00	4.07	4.05	3.00	15.40
$[CuL^2(OH)(H_2O)].6H_2O$	608.5	65.2	35.85	35.29	6.30	6.10	4.65	4.66	1.63	46.00

$\Lambda^* = \upsilon^{-1}\ cm^2mol^{-1}$, BM= Bohr magneton

Infrared spectra of the chelates

The infrared spectra of the chelates under investigation (Table2) were compared with that of the free Schiff bases to determine the changes that might have taken place during the complexation. IR spectral values of the valine and tyrosine Schiff base chelates display bands in the range of 1597-1619 and 1519-1595cm^{-1} assignable for ν(C=N) and ν(-CO_2) groups [7, 8]. A slight shift to lower or higher frequency is observed for ν(C=N) and ν(-CO_2) bands after complexation. The appearance of new bands in the range of 592-672cm^{-1} and 416-515cm^{-1} which are due to ν(M-O) and ν(M-N) bonding supports the involvement of the oxygen of the carboxylic group and nitrogen atom of azomethine group of both Schiff bases in complexation.[9] A broad band with the range 3332-3449cm^{-1} confirms the presence of water molecules in the separated chelates[10].

Table-2: Infrared (cm^{-1}) and electronic spectral data of Schiff base and chelates

Schiff base / Chelates	υCO_2^-	υOH	υC=N	υM-O	υM-N	UV(nm)
Valine Schiff Base (L^1)	-	3337	1588	-	-	253
Tyrosine Schiff base (L^2)	3017	-	-		-	339
$[VOL^1(H_2O)_2]$	1542	3422	1596	592	515	402
$[NiL^1(OH)(H_2O)_2].6H_2O$	1585	3332	1628	655	416	338
$[CuL^1(OH)(H_2O)_3].7H_2O$	1595	3448	1619	672	472	337
$[VO(L^2)_2(H_2O)].H_2O$	1590	3472	1613	649	432	362
$[NiL^2(OH)(H_2O)_3].10H_2O$	1552	3350	1602	634	467	339
$CuL^2(OH)(H_2O)].6H_2O$	1519	3449	1597	635	487	339

Electronic spectra and magnetic moments

The electronic spectral data of the Schiff base (Table-2) exhibit π→π*(Phenyl ring) and n→π* (HC=N, -OH, CO_2H). The electronic spectra of VO-L^1 and VO-L^2

Schiff base chelates show two bands at 402 and 362nm due to $^2T_2g \rightarrow {}^2Eg$ transition. The observed bands and the magnetic moment values of 1.27 and 1.53BM suggest the existence of an octahedral geometry.[11] The electronic spectrum of Ni(II)-L^1 Schiff base chelate exhibits a band at 338 assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition. The nature of the band and the magnetic moment value of the chelate (2.08BM) support the existence of an octahedral structure. For Ni(II)-L^2 Schiff base chelate, the spectrum shows three bands at of 287, 393 and 339nm attributed to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions. These data suggest the presence of an octahedral geometry. The magnetic moment of the chelate (3.00 BM) and the intensity of the bands support the mentioned structure.[12] The electronic spectra of Cu-L^1 and Cu-L^2 Schiff base chelates show two bands at 337 and 339 nm which are due to $^2E_g \rightarrow {}^2T_{2g}$ transition. Based on the nature of the bands and the magnetic moment values of 1.28 and 1.63BM, an octahedral and a square planar configurations were suggested.[13]

Electron paramagnetic resonance spectra

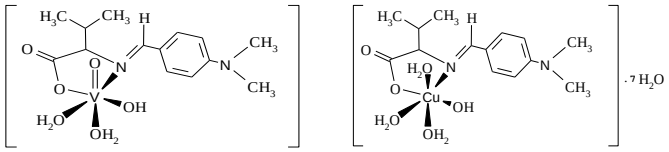
In the present investigation, the electron paramagnetic resonance spectral data of the Schiff base chelates are lied between 1.9992 and 2.1537, and the obtained data showed an octahedral geometry for VO(IV), Ni(II) and Cu(II) chelates and a square planar geometry for Cu-L^2 chelate.[14]

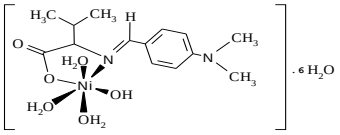
Conclusion

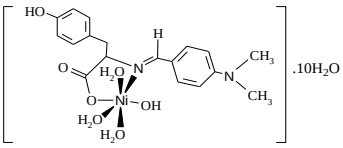
From the previous chemical analyses [elemental analysis, molar conductance measurements, magnetic moment measurements, infrared, electronic and electron paramagnetic resonance],

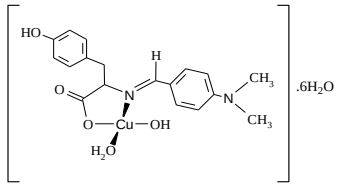
the geometrical structures of the prepared chelates are given below:

1:1 [M:L] chelates

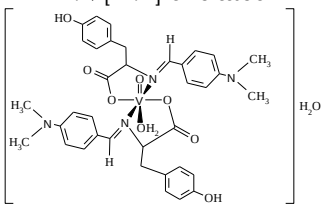








1:2 [M:L] chelates



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