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Amino Acid Schiff Base Complexes of Mn(II),Co(II),Ni(II),Cu(II) and Cd(II) Transition Metal Ions

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Summary: The preparation and investigation of a new Schiff base ligand containing L-phenylalanine and salicylaldehyde have been done. The reaction of L-phenylalanine with salicylaldehyde leads to the isolation of amino acid Schiff base (L). The reaction of divalent transition metal ions with (L) gives $Na_2[M(L)_2]nH_2O$ complexes (where M = Mn, Co, Ni, Cu or Cd and n= 3, 5.5, 6, 6.5 or 7). The ligand and its complexes were characterized by physical and spectroscopic measurements. These complexes are coordinated through the ONO donor set derived from the carboxyl, imino and phenoxy groups of the ligand.

Introduction

The Salicylaldehyde and L-phenylalanine ligands are bidentate and form several complexes with transition and non-transition metal ions. Salicylaldehyde compounds have variety of applications in chemistry and medicine.(1) Long et. al.(2) synthesized and characterized complexes of divalent metal ions (Mn, Ni, Cu and Zn) with 1,3-bis(4-methyl-5-imidazol-1-yl)ethylideneamine propan-2-ol. The Mn(II), Ni(II) and Cu(II) complexes exhibited an octahedral geometry, meanwhile, the Zn(II) complex displayed a distorted square-pyramidal coordination structure. The complexes of $Fe(SalPnL^-)$-ClO_4, (L^- is 2,2-bipyridyl or, o-phen, (H_2SlPn) or N,N-bis(salicylidene)propylene-diamine and $[Fe(SalPn)_2L^1]$, L^1 is terephthalate or fumarate dianions have been prepared and studied by elemental analysis, infrared and electronic spectroscopies and magnetochemical measurements. An octahedral arrangement of Fe(III) complex was suggested.(3) New unsymmetrical Ni(II)-Schiff base complex derived from o-phenylene, benzoylacetone and salicylaldehyde have been synthesized and investigated using a different physical techniques, such as; elemental analysis, infrared, electronic, proton nuclear magnetic resonance spectroscopies. The elemental analysis data show the

presence of 1:1 [M:L] complex and an octahedral geometry was proposed basis on the previous analyses.[4] Ben saber et. al.[5] prepared and investigated some Schiff base chelates derived from 4-dimethylaminobenzaldehyde and 2-aminobenzoic acid of Cr(III), Fe(III), Co(II), Ni(II) and Cu(II) ions. The used physical techniques exhibit one chelation mode through the nitrogen atom of the azomethine and COOH group. An octahedral geometry was suggested for Cr(III) and Fe(III) chelates and a square planar was proposed for the other chelates. Two copper (II) tripeptide Schiff base complexes of the type $[Mg(H_2O)_6][CuL^*]_2 3.5H_2O$ and $[Cd(H_2O)_4][CuL^*]_2.3.5H_2O$; (L* is N-salicylideneglycylglycine) have been synthesized and structurally characterized.[6] A series of manganese(III) complexes of amino acid Schiff bases was synthesized from 2-hydroxy-1-naphthaldehyde,L-serine, L-methionine and L-cystein. The structure of their metal complexes was investigated by elemental analyses, IR, TGA, magnetic susceptibility and mass spectra.[7]

The aim of this investigation is to elucidate the chemical structures of the prepared Schiff base complexes.

Experimental

Chemicals and reagents

All chemicals used in this work were laboratory pure including salicylaldehyde, L-phenylalanine, $MnCl_2.4H_2O$, $Co(AcO)_2.4H_2O$, $Ni(AcO)_2.4H_2O$, $Cu(AcO)_2.H_2O$, $Cd(AcO)_2.2H_2O$, NaOH, C_2H_5OH , CH_3OH, DMF and double distilled water.

Preparation of Schiff base

The amino acid Schiff base was prepared as follows: sodium hydroxide (10 mmol, 0.4 g) was dissolved in methanol (25 cm^3) and the amino acid (L-phenylalanine); 10 mmol was added to it. The mixture was stirred magnetically at room temperature. When the mixture becomes homogeneous, (a 10 mmol, 1.22 g) of salicylaldeyde (25 cm^3) was added. After 2 minutes the mixture 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, recrystallized from hot

methanol to give yellow crystals and dried at ambient temperature with 73% yield and its purity was confirmed by TLC technique.

Preparation of complexes

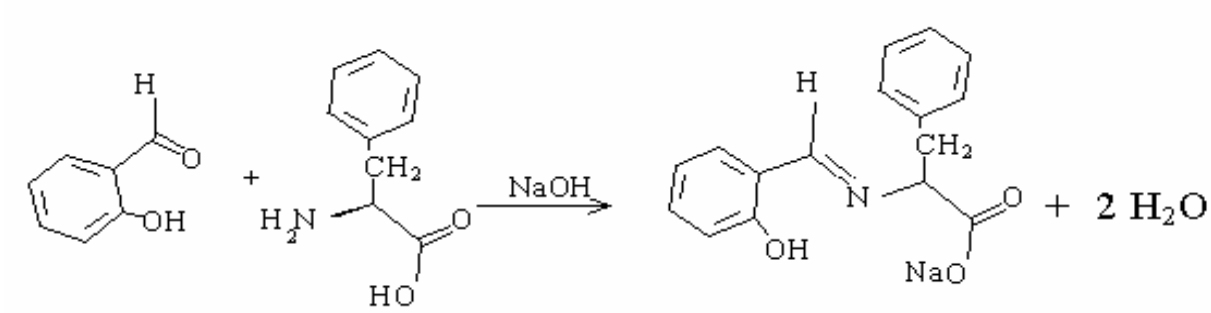
A methanolic solution (50 cm^3) of salicylaldehyde (20 mmol, 2.44 g) containing NaOH (20 mmol, 0.8g) was added to the L-phenylalanine (0.02 mole, 3.30g). After 2 minutes, the solids of the metal salts [10 mmol, $MnCl_2.4H_2O$ (1.98 g), $Co(AcO)_2.4H_2O$ (2.49 g), $Ni(AcO)_2.4H_2O$ (2.48 g), $Cu(AcO)_2.H_2O$ (1.99 g) and $Cd(AcO)_2.2H_2O$ (2.67 g)] were added, stirred magnetically for 3 h and the solution volume was reduced to 75% by evaporation and the residue was left to stand overnight. The solids were obtained by filteration and recrystallized from a methanol/ethanol (50%) mixture.

Apparatus

The chemical analyses (C, H and N) were performed in advanced laboratory of chemical analysis, Ras–Lanouf Company, Libya. The thermogravimetric analysis was achieved using Schimadzu thermal analyzer (Japan). The weight losses were measured from ambient temperature up to 1000 $^{\circ}C$ in a rate of 10 $^{\circ}C$ per minute. Infrared spectra were recorded using KBr disc technique on IFS-25 DPUS/IR spectrometer (Bruker). The electronic spectra were measured by using a Perkin–Elmer lambda 4B spectrophotometer.

Results and Discussion

The reaction of salicylaldehyde with L-phenylalanine in methanol yields one amino acid Schiff base compound. The chemical equation concerning the formation of the compound represented as follows:



Salicylaldehyde ***L-phenylalanine*** ***Schiff base***

Microanalysis

The elemental analyses (C, H and N) of the amino acid Schiff base and their complexes are listed in table (1). The empirical formulae of the complexes indicate the formation of a 1:2 [M: L] ratio and they exist as Na salt. Furthermore, the calculated elemental analyses are in a good agreement with the found values.

Thermogravimetric analysis

The thermogravimetric analysis data of Mn(II) L-phenylalanine Schiff base complex show a weight-loss 14.31% within the 30-440 ^{o}C range, interpreted as being due to loss of moisture and hydrated water molecules during the complex drying process, whereas, the second weight-loss 25.26% within the 440-530 $^{\circ}$C range is attributed to the decomposition of organic components of free Schiff base. The residual metal oxide% coincides fairly with the theoretical value table (1). On the basis of the above observations, the following scheme for thermogravimetric decomposition is proposed:

$$Na_2[Mn(L)_2]\ 6H_2O \xrightarrow{30\text{-}265\ ^{o}C} Na_2[Mn(L)_2] + 6H_2O$$

$$\text{Intermediate (unstable)} \longrightarrow Na_2[Mn(L)_2] \xrightarrow{265\text{-}450\ ^{o}C} \text{Intermediate} \xrightarrow{> 450\ ^{o}C} \text{Metal oxide (MnO, } MnO_2\text{)}$$

Intermediate = Decomposition of organic ligand.

Table 1: Elemental analyses, molecular weights, molar conductance and thermogravimetric analysis of the Schiff base and its complexes.

Schiff base/Complexes	**C%**	**H %**	**N%**	**M.W**	**%H_2O**	**MnO+ MnO_2**
NaH L .1.5 H_2O	60.00 **(60.37)**	6.28 **(5.35)**	5.47 **(4.40)**	318.00		
$Na_2[Mn(L)_2]$ 6 H_2O	51.74 **(51.76)**	5.16 **(4.99)**	4.03 **(3.77)**	741.93	14.31 **(14.55)**	25.26$^{\#}$ **(24.90)**
$Na_2[Co(L)_2]$ 6.5 H_2O	50.63 **(50.86)**	4.71 **(5.03)**	3.70 **(3.71)**	754.93		
$Na_2[Ni(L)_2]$ 3 H_2O	43.16 **(43.16)**	5.25 **(5.95)**	2.87 **(3.15)**	889.69		
$Na_2[Cu(L)_2]$ 7 H_2O	50.12 **(49.99)**	4.93 **(5.07)**	3.73 **(3.64)**	768.54		
$Na_2[Cd(L)_2]$ 5.5 H_2O	48.46 **(48.58)**	4.68 **(4.55)**	3.50 **(3.54)**	790.40		

( ) Calculated values

$^{\#}$ as last M.Wt

Infrared spectra

Table -2 shows the infrared band assignments of the free amino acid Schiff base and its complexes. A band at 1624 cm^{-1} is due to the presence of azomethine group (-C=N) of the free ligand. This band is shifted slightly to higher frequency on complex formation. A broad band at 3406 cm^{-1} was observed in the spectrum of the free ligand. Whereas, the spectra of the prepared complexes also display abroad band at 3406-3533 cm^{-1} range corresponding to the presence of water molecules.[8] A band at 1589 cm^{-1} is assigned to (C=O) of ($-COO^-$) group.[9] This band is changed during the complex formation indicating its participation in chelation with the metal ions under investigation.[10] New bands at 643 - 686 and 429-497 cm^{-1} which do not exist in the free ligand are attributed to ν(M-O) and ν(M–N) vibrations. The above observations explain the involvement of azomethine (-C=N) and (-OH, C=O of –COOH) groups in chelation with metal ions.[11]

Electronic spectra

The electronic spectra of the free ligand and its complexes were recorded in DMF solvent and their band assignments are shown in table-2. The L-phenylalanine Schiff base spectrum shows two bands at 216 and 288 nm (46296 and 34722 cm^{-1}) due to π-π^* of phenyl group and n-π^* of -C=N group.[12] The electronic absorption spectrum of Mn(II) complex shows a band at 371 nm (26954 cm^{-1}) which is attributed to $^2A_{2g} \rightarrow {}^2T_{1g}$ transition. The intensity of the band suggest an octahedral geometry for Mn (II) complex.[13] The electronic spectrum of Co(II) complex of the type $Na_2[Co(L)_2].4H_2O$ exhibits bands at 385-766 nm (25947-13055 cm^{-1}) range due to $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (F) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions. These data suggest the presence of an octahedral geometry.[14] The electronic absorption spectrum of Ni(II) complex exhibits two bands at 379 and 775 nm (26385 and 12903cm^{-1}) The first band is attributed to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition and the other one is due to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition. The intensity of these two bands supports an octahedral structure.[15] Also the spectrum of Cu(II) complex exhibits a band at 378 nm (26455 cm^{-1}) due to $^2E_g \rightarrow {}^2T_{2g}$ transition. An octahedral geometry was proposed.[16] A Cd(II) ion has $4d^{10}$ electronic configuration of ^1S ground term. The spectrum of Cd(II) complex shows bands in the range of 383-564 nm (26110-

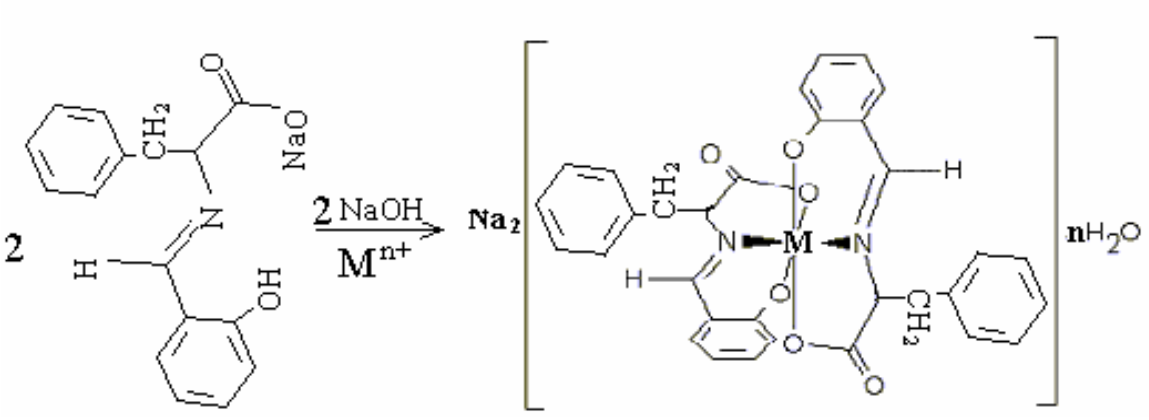
17730 cm^{-1}) which could be attributed to the presence of a charge transfer band. It has pointed out, that, a metal ion is capable of forming L → M charge transfer due to the existence of empty $5d^0$ orbital leading the bonding to take place by the acceptance of a lone pair of electrons from the donor nitrogen atom of the ligand under investigation.[17]

Table 2: Infrared band assignments (cm^{-1}) and electronic spectral data (**nm**, cm^{-1}) of the Schiff base and its complexes.

Schiff base/Complexes	υ(OH) (H_2O)	υ(C=N)	υ(COO)	υ(M-N)	υ(M-O)	λ_{max}nm	cm^{-1}
NaH L .1.5H_2O	3406	1624	1589	-	-	**216-288**	46296-34722
$Na_2[Mn(L)_2]$ 6H_2O	3406	1639	1585	489	686	**371**	26954
$Na_2[Co(L)_2]$ 6.5H_2O	3419	1644	1600	467	670	**385-766**	25947-13055
$Na_2[Ni(L)_2]$ 3H_2O	3533	1650	1612	443	667	**379-775**	26385-12903
$Na_2[Cu(L)_2]$ 7H_2O	3428	1632	1602	497	643	**378**	26455
$Na_2[Cd(L)_2]$ 5.5H_2O	3429	1633	1579	429	672	**383-564**	26110-17730

Conclusion

From the previous chemical analyses, one can suggest the following chemical structure



The formation of M(II)- L-phenylalanine Schiff base complexes

(M = Mn , Co, Ni, Cu and Cd)

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