

Synthesis and Characterization of Copper (II), Zinc (II), Cobalt (II) and Nickel (II) complexes Derived from 2-Hydroxy-1-naphthaldehyde and DL-glycyl-DL-glycine

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الخلاصة:

تم تحضير معقدات النحاس، الزنك، الكوبلت، النيكل الثنائية مع قاعدة شف المشتقة من 2- هيدروكسي-1- نفتالديهايد و كلايسين- كلايسين. تم تشخيص هذه المركبات بواسطة استخدام التحليل الدقيق للعناصر والتوصيلية المولارية. كذلك تم استخدام التقنيات الطيفية مثل الأشعة ما تحت الحمراء والأشعة فوق البنفسجية – المرئية. بينت قياسات التوصيلية المولارية أن المعقدات الثنائية هي بنسبة 1:1 وغير الكتروليتية. كذلك بينت الأشعة ما تحت الحمراء الارتباط الرباعي لليكاند. ان امتطاط حزم مجموعة الكربوكسيليت في أطيف الأشعة ما تحت الحمراء بينت أن هذه المجموعة تلعب كمجموعة أحادية المنح عندما ترتبط بالفلز.

مواقع الارتباط هي اوكسجين مجموعة الكربوكسيليت، نايتروجين مجموعة C=N، نايتروجين مجموعة الامايد، و اوكسجين الفينولية.

Abstract:

Copper (II), Zinc (II), Cobalt (II) and Nickel (II) complexes with the Schiff base derived from 2-Hydroxy-1-naphthaldehyde and DL-glycine -DL-glycine were synthesized. These compounds have been characterized by elemental analysis, conductivity measurement, IR and UV-Vis. The molar conductance measurement indicate that the complexes are 1:1 non-electrolytes. The IR data demonstrate the tetradentate binding of the ligand. The COO⁻ stretching bands in the IR spectra suggest that carboxylate acts as a monodentate group when binding with metal. The bonding sites are the carboxylate oxygen, imino nitrogen, amide nitrogen, and phenolic oxygen.

KEYWORDS: Dipeptide, Schiff base, IR, Glycyl-glycine, UV-Vis

Introduction :

The coordination chemistry of amino acid Schiff base is of considerable interest due to their biological importance (1,2). N-salicylideneamino acid complexes may serve as models for N-pyridoxylideneamino acid complex systems which are believed to be the intermediates in the transamination process (3). The coordination of a metal ion to such Schiff bases stabilizes the azomethine linkage. under conditions that would otherwise promote cleavage (4-6). In addition the complexes of amino acid Schiff base are considered to be a new kind of potential antibacterial and anticancer reagents (7,8). Metal complexes with Schiff bases of amino

acids and diverse carbonyl compounds such as pyridoxal, salicylaldehyde, camphor derivatives, pyruvic acid and acetylacetone are known (9-12). System in which the Schiff bases of amino acids are derived from β-diketones have received scant interest (13-15). Neglect of this ligand type of β-ketoimine – N-alkanoic acid seems to arise from their known hydrolytic instability (16). Furthermore, those metal complexes primarily have been confined to transition elements. N-benzoylacetoneglycine has been stabilized in the form of its sodium salt and the complexes of this ligand with a series of lanthanide (III) ions have been prepared and

their antioxidative actions also have been determined (17).

However, little attention has been paid to systems in which the Schiff bases derived from simple peptides. A vanadium complex $\text{VO}(\text{sal} - \text{glygly})(\text{H}_2\text{O})_n$ ($\text{sal} - \text{glygly} = \text{N-salicylidene-glycylglycine}$); $n=1.5 - 3.0$ has been isolated from relatively concentrated solutions containing oxovanadium (IV), glycylglycine and salicylaldehyde (18). Synthesis, crystal structure and magnetic studies of *cis*-configuration copper (II) - M(II) (M = Ba, Ca) complexes of the *sal*-glygly Schiff base were determined (19). We have prepared and characterized the uranyl complexes of Schiff base obtained by condensing glygly with hydroxybenzaldehyde (20). Recently, two copper (II) tripeptide Schiff base complexes: $[\text{Mg}(\text{H}_2\text{O})[\text{CuL}]2.3.5\text{H}_2\text{O}$ and $[\text{Cd}(\text{H}_2\text{O})_4(\text{CuL})_2].3.5\text{H}_2\text{O}$ ($\text{H}_3\text{L} = \text{N-sal} - \text{glygly}$) have been synthesized and structurally characterized (21). Also, reaction of $\text{Na}[\text{CuL}]$ (where $\text{H}_3\text{L} =$ the Schiff base derived from 5-bromo salicylaldehyde and glygly) with $\text{La}(\text{NO}_3)_3$ leads to the formation of carboxylate-bridged polynuclear copper (II) - lanthanide (III) rings of formula $[\text{Ln}(\text{H}_2\text{O})_5(\text{CuL})_2][\text{CuL}]. 8\text{H}_2\text{O}$ ($\text{Ln} = \text{La}$ and Ce) (22).

In continuation of our interest the coordination behavior of Schiff base of the biologically important glycylglycine, we report the synthesis and characterization of a series of Copper (II), Zinc (II), Nickel and Cobalt (II) complexes of Schiff base obtained by condensing glycylglycine with 2-Hydroxynaphthaldehyde. The Schiff base and the complexes were characterized using: elemental analysis; conductivity measurements, UV-Vis, and IR.

Materials and Methods :

Reagents and apparatus. The dipeptide, glycylglycine was purchased from Fluka (LTD) and used without further purification. 2-Hydroxy-1-naphthaldehyde were obtained from Fluka and metal acetate was obtained from Merck (LTD). All other reagent and solvent were purchased from commercial sources and were of analytical grade. Solvent were purified and dried by standard methods. Elemental analysis was done using a Perkin-Elmer elemental analyzer. IR spectra were recorded in KBr disc on a (8300)(FT-IR) Shimadzu spectrophotometer in the range $4000-400 \text{ cm}^{-1}$ region. The electronic spectra were recorded on a Shimadzu, 160, using a quartz cell of (1.0) cm length spectrophotometer. Molar conductance of the complexes was measured in methanol (10^{-3}) solution using a coronation digital conductivity meter.

Synthesis of the Dipeptide Schiff base Potassium Salt (23)

A solution containing (5mmol) of glycylglycine in 20 ml of water was added to 15 mL of an ethanol solution containing (5 mmol) of KOH. The resulting solution was stirred on a water bath at 25°C for half an hour and then filtered. The filtrate was added dropwise to 20 mL of an ethanol solution of 2-Hydroxy-1-naphthaldehyde (5 mmol) with stirring on a water bath at 25°C for one hour. The volume of the solution was reduced by distillation to 5 mL and then ethanol (10 mL) was added. The yellowish precipitate formed was removed by filtration. The precipitate was recrystallized from methanol.

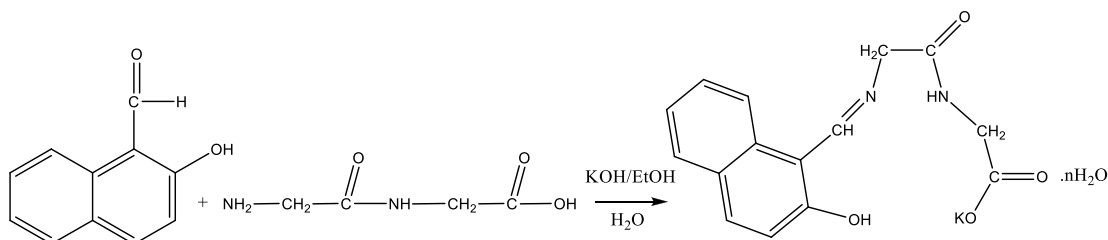


Fig.1 Synthesis and structure of Schiff base ligand

Synthesis of Schiff base complexes(23) .

The metal acetate (5mmol) was dissolved in 20 mL of water . The solution was filtered and added dropwise into 25 mL of an ethanol solution of the Schiff base (5mmol). The reaction mixture was stirred at 25 C° on water bath for 3 h. The resulting precipitate was filtered , washed with ethanol and ethyl ether . and was recrystallized from methanol , and then dried in vacuum desiccator . The analytical data are summarized in Table 1.

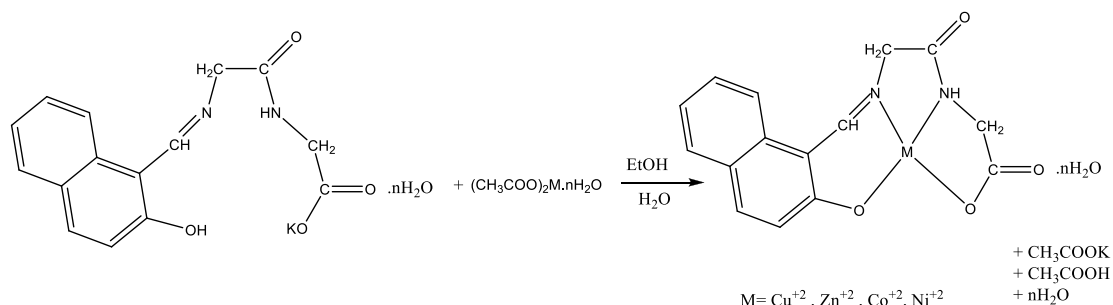


Fig. 2 Synthesis and proposed structures of complexes

Results and Discussion :

The physical properties and analytical data of the ligands and their complexes are given in Table 1. Elemental analysis data of the complexes are in good agreement with theoretical values. The analytical data (Table 1) indicate that the metal to ligand ratio is 1:1 in all the complexes systems and it can be (24).

represented as $(L.nH_2O)$, where L is the Schiff base ligand obtained by the condensation of 2-Hydroxynaphthaldehyde with glycylglycine. The measured molar conductance values for methanol solutions of the prepared complexes are in the $(8.3 - 24.5) \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ range. This suggests a non-electrolytic nature for the complexes

Compounds	Formula	Mol. Wt.	M.p (C°)	Yield (%)	Conductivity Ohm ⁻¹ cm ² mol ⁻¹	Found (calc.) (%)			
						C	H	N	M
KHL.2H ₂ O	C ₁₅ H ₁₇ KN ₂ O ₆	360.40	134	35	–	49.89 (49.99)	4.68 (4.75)	7.56 (7.77)	–
CuL.2H ₂ O	C ₁₅ H ₁₆ N ₂ O ₆ Cu	383.84	254	66	17.7	46.79 (46.94)	4.04 (4.20)	7.23 (7.30)	16.65 (16.56)
ZnL.2H ₂ O	C ₁₅ H ₁₆ N ₂ O ₆ Zn	385.71	> 265	68	8.3	46.44 (46.71)	4.37 (4.18)	7.39 (7.26)	16.89 (16.96)
NiL.4H ₂ O	C ₁₅ H ₂₀ N ₂ O ₈ Ni	415.02	188	63	24.5	43.11 (43.41)	4.75 (4.86)	6.63 (6.75)	14.06 14.14(
CoL.3H ₂ O	C ₁₅ H ₁₈ N ₂ O ₇ Co	397.25	243	60	23.6	45.14 (45.35)	4.37 (4.57)	6.91 (7.05)	14.76 (14.84)

Table 1. Physical and analytical data of the Schiff base ligands and their complexes

Infrared Spectra :

Table 2 lists some pertinent IR frequencies for the potassium salt of the ligand and its complexes together with our proposed assignments . The IR spectra of the Cu(II) , Zn(II) ,Ni(II) and Co(II) complexes and the potassium salt of the ligand exhibit a strong and broad band in the region 3309 – 3414 cm⁻¹, which can be attributed to the stretching vibration of the water molecules (25). The C=N imine stretching mode is observed at 1627 cm⁻¹ for the potassium salt of the ligand , clearly indicating formation of the Schiff base . When the spectra of the complexes are compared with those of the potassium salt of the Schiff base ligand , the $\nu(\text{C}=\text{N})$ bands is shifted to lower or higher frequency . indicating that the imino nitrogen is coordinated to the metal ion .

In spectra of the complexes , the antisymmetric carboxyl stretching absorptions shifted to higher or lower frequency and symmetric carboxyl stretching shifted to lower frequency , indicating the formation of a

linkage between metal ion and carboxylate oxygen (10) . The asymmetric and symmetric carboxyl stretching absorption observed for the complexes are close to 1590 and 1400 cm⁻¹, respectively , affording a $\Delta\nu(\nu_{\text{as}} - \nu_{\text{s}})$ value of 164-162 cm⁻¹, characteristic of formation behaviour(25) .

Characteristic absorption bands appear at 1213 and 1541 cm⁻¹. These may be assigned to phenolic C-O and amide stretching vibrations for the potassium salt of the ligand , respectively . The phenolic stretching C-O and amide are shifted to higher or lower frequency, implying that the phenolic oxygen and amide nitrogen on the peptide chain are coordinated to the metal ion.

In the low- frequency region , two bands at 511 and 543 cm⁻¹ are , respectively , assigned to $\nu(\text{M}-\text{N})$ (imino nitrogen) and $\nu(\text{M}-\text{N})$ (amide nitrogen). Two bands at 414 and 540 cm⁻¹ are attributed respectively to $\nu(\text{M}-\text{O})$ (phenolic oxygen) and $\nu(\text{M}-\text{O})$ (carboxylate oxygen (25)).

Table.2. Infrared Spectral Data(cm^{-1})

Compound	OH ν	C=N ν	$\nu_{\text{as}}\text{COO}^{\nu}$	(CONH) ν	$\nu_{\text{sym}}\text{COO}^{\nu}$	C-N ν	C-O ν	δ_{COO^-}	M-O ν	M-N ν
KHL.2H ₂ O	3309 m.br	1627 m	1591 m	1541 m	1427 m	1398 m	1213 m	748 m	-	-
CuL.2H ₂ O	3410 m.br	1595 s. sh	1548 w	1521 w	1396 w	1365 w	1228 w	767 w	513w 459w	437w 414w
ZnL.2H ₂ O	3410 s.br	1631 s.sh	1543 w	1454 m	1408 w	1365 w	1195 w	759 s	540w 511w	439w 420w
NiL.4H ₂ O	3414 s.br	1647 s.sh	1539 w	1516 m.sh	1396 m	1365 m	1230 w	767 m	543w 516m	451m 428m
CoL.3H ₂ O	3414 m.br	1643 s.sh	1593 m.sh	1543 m.sh	1431 w	1400 m.sh	1211 w	744 m	543w 524w	478m 455w

Electronic Spectra :

The electronic spectral data of the synthesized complexes in methanol solution are given in Table 3. The UV spectra of the Schiff base exhibit four bands of strong intensity at 304 , 320 , 401 , and 416 nm , these bands are associated with $\pi-\pi^*$ transition .the first and second with those of the naphthalene ring and the third and fourth with those of the imino group (1) . In complexes the imino $\pi-\pi^*$ transition is shifted to higher wave length as a consequence of coordination when binding with the metal. The Copper (II) , Nickel (II) and Cobalt (II) has a d-d bands suggesting that it is a tetra-coordinated complex (26) . Finally, on the basis of the elemental data which afford the general formulation ML.nH₂O and the IR and UV data obtained for the complexes , we can deduce that the dipeptide Schiff base ligand is coordinated to the central metal as a tetradentate O-N-N-O ligand where two five – membered rings and six – membered ring are formed . The bonding sites are the carboxylate oxygen , imino nitrogen , amide nitrogen , and phenolic oxygen, and the suggested structure is shown in Fig. 2.

Table.3. Electronic Spectral Data(nm)

Compounds	λ_{max} nm				
KHL.2H ₂ O	304	340	401	416	-
CuL.2H ₂ O	214	304	330	415	708, 784
ZnL.2H ₂ O	219	315	407	-	-
NiL.4H ₂ O	304	335	410	470	660 , 726
CoL.3H ₂ O	301	334	400	485	741

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