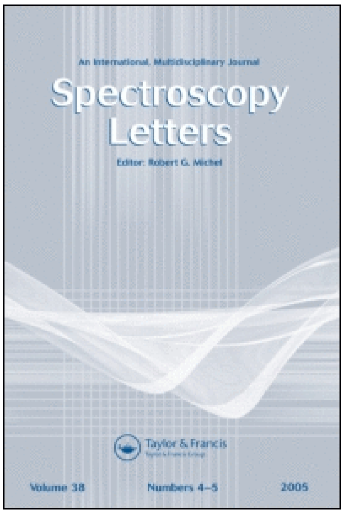

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Studies on Cu(II), Zn(II), Ni(II) and Co(II) complexes derived from two dipeptide Schiff Bases

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To cite this Article Guangbin, Wang(1999) 'Studies on Cu(II), Zn(II), Ni(II) and Co(II) complexes derived from two dipeptide Schiff Bases', Spectroscopy Letters, 32: 4, 679 — 688

To link to this Article: DOI: 10.1080/00387019909350017

URL: http://dx.doi.org/10.1080/00387019909350017

SPECTROSCOPY LETTERS, 32(4), 679–688 (1999)

Studies on Cu(II), Zn(II), Ni(II) and Co(II) complexes derived from two dipeptide Schiff Bases

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Abstract

Some new metal complexes of two dipeptide Schiff bases derived from salicylaldehyde and dipeptides such as glycyl-DL-alanine and glycyl-DL-phenylalanine have been synthesized and characterized by elemental analysis, molar conductance, IR, UV spectra, TG and DTA studies. The COO stretching bands in IR spectra suggest that the carboxylate acts as a monodentate group when binding with metal. The ligands are coordinated to the central metal as tetradentate ligands. The bonding sites are the carboxylate oxygen, imino nitrogen, amide nitrogen and phenolic oxygen.

Key words: Dipeptide Schiff base, complex, synthesis, spectral characterization

Introduction

N-Pyridoxylideneamino acid Schiff bases are key intermediates in a variety of metabolic reactions involving amino acids, such as decarboxylation, transamination, racemization, and C-C bond cleavage(1). Metal ions catalyze the reactions involving vitamin B_6. These results seem to indicate that metal complexes of Schiff bases derived from various amino acids are formed as intermediates(2,3). N-salicylideneamino acid complexes may serve as models for N-pyridoxylideneamino acid complex systems(4-8). In addition, N-salicylideneamino acid complexes are found to exhibit potential anticancer, antibacterial and antifungal activity(9,10).

In the present work we have prepared and characterized copper(II), zinc(II), nickel(II) and cobalt(II) complexes of two new dipeptide Schiff bases derived from salicylaldehyde and dipeptides such as glycyl-DL-alanine and glycyl-DL-phenylalanine. The peptide function presented in Schiff bases provides interesting new possibilities for the coordination of metal.

Experimental

Materials

All chemicals used throughout this investigation were of reagent grade.

Synthesis of the dipeptide Schiff bases

The potassium salt of Schiff bases was prepared according to a general method. A solution containing 5 mmol of glycyl-DL-alanine (or glycyl-DL-phenylalanine) in 20 cm^3 of water was added to a 15 cm^3 of an alcoholic solution containing 5 mmol (0.28 g) KOH. The resulting solution was stirred at 25° C for half an hour and then filtered. The filtrate was added dropwise to a 20 cm^3 of an ethanol solution of salicylaldehyde (5 mmol) and was stirred at 25° C for one hour. The yellowish solution was reduced by

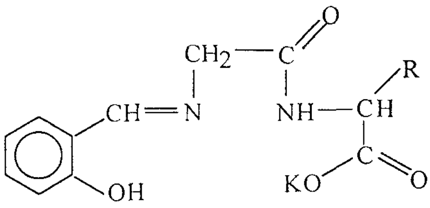

Fig. 1 Structure of the potassium salt of the ligands

R = CH_3, KH(SGA); R = CH_2Ph, KH(SGP)

distillation to 5 cm^3 under nitrogen and then ethanol (10 cm^3) was added. The volume of the yellowish precipitate formed was removed by filtration. The precipitate was recrystallized from methanol. KH(SGA).H_2O, with a melting point of 114 °C, KH(SGP).H_2O, with a melting point of 71 °C.

Synthesis of complexes

The following general procedure was used for the preparation of the complexes. Metal acetate (5 mmol) was dissolved in 25 cm^3 of water, filtered, and added dropwise into the ethanol solution of the Schiff base (5 mmol). The reaction mixture was stirred at 25 ° C for three hours. The precipitate was filtered, washed with ethanol and ethyl ether, and then dried in a vacuum desiccator. The analytical data are summarized in Table I.

Physical measurements

Carbon, hydrogen and nitrogen analyses were obtained using a Yanaco Chn Corder MT-3 elemental analysis instrument. The contents of the metals were determined by the standard literature procedures(11). Conductivities of 10^{-3} M solution of the complexes were measured in methanol at 25° C using a DDS-11A apparatus (Shanghai, China). The electronic spectra were recorded in methanol on a Shimazdu UV-260 spectrophotometer. The infrared spectra were recorded in the form of KBr pellets on a Nicolet 5DX infrared fourier transform spectrometer. Thermogravimetric (TG) curves were obtained in static air using a LCT differential thermal balance (Beijing Optical

Table I. Analytical and physical data

Compound	Yield(%)	Color	Found (Calcd.)%			Conductivity	
			C	H	N	M	$(ohm^{-1} cm^2 mol^{-1})$
KH(SGA).H_2O $KC_{12}H_{15}N_2O_5$	53	Yellow	46.60 (47.04)	4.81 (4.94)	9.23 (9.15)	---	---
Cu(SGA).$2H_2O$ $CuC_{12}H_{16}N_2O_6$	58	Green	41.08 (41.44)	4.56 (4.64)	7.90 (8.06)	18.39 (18.27)	12.3
Zn(SGA) $ZnC_{12}H_{12}N_2O_4$	65	Light yellow	45.83 (45.96)	3.69 (3.86)	8.69 (8.93)	20.62 (20.85)	11.7
Ni(SGA). $4H_2O$ $NiC_{12}H_{20}N_2O_8$	54	Light yellow	38.31 (38.03)	4.99 (5.32)	7.49 (7.39)	15.36 (15.49)	25.6
Co(SGA) $CoC_{12}H_{12}N_2O_4$	52	Light brown	46.48 (46.92)	4.08 (3.94)	9.06 (9.12)	19.31 (19.19)	14.2
KH(SGP).H_2O $KC_{18}H_{19}N_2O_5$	55	Yellow	56.66 (56.53)	5.12 (5.01)	7.58 (7.33)	---	---
Cu(SGP).H_2O $CuC_{18}H_{18}N_2O_5$	78	Green	52.95 (53.26)	4.25 (4.47)	7.02 (6.90)	15.48 (15.66)	8.2
Zn(SGP).H_2O $ZnC_{18}H_{18}N_2O_5$	76	Light yellow	52.83 (53.02)	4.34 (4.45)	6.77 (6.87)	16.27 (16.04)	12.3
Ni(SGP). $2H_2O$ $NiC_{18}H_{20}N_2O_6$	75	Light yellow	51.18 (51.59)	4.69 (4.81)	6.72 (6.69)	13.87 (14.01)	22.1
Co(SGP).$2H_2O$ $CoC_{18}H_{20}N_2O_6$	81	Light brown	51.30 (51.56)	4.63 (4.81)	6.45 (6.68)	14.19 (14.05)	14.2

Instrument Factory). The heating rate was 10° C min^{-1}. Differential thermal analysis (DTA) was performed using a LCT differential thermal balance (Beijing Optical Instrument Factory) under the same condition as the TG curve, using α-Al_2O_3 as the reference.

Results and discussion

The elemental compositions are given in Table I. The results suggest the general molecular formula M(SGA).nH_2O and M(SGP).nH_2O for the synthesized complexes.

The measured molar conductance values for the methanol solutions of prepared complexes are in the 8.2-25.6 ohm^{-1} cm^2 mol^{-1}range. This suggests non-electrolytic nature for the complexes(12).

The data of the thermogravimetric analysis (TG) and differential thermal analysis (DTA) are shown in Table II, indicating that Cu(SGP).H_2O and Zn(SGP).H_2O contain only one molecule of water of crystallization, but Cu(SGA).$2H_2O$, Ni(SGP).$2H_2O$ and CO(SGP).$2H_2O$ contain two molecules of water of crystallization, and Ni(SGA).$4H_2O$ contain four molecules of water of crystallization, supporting the suggested formula of the complexes(10,13).

Infrared spectra

Table III lists important IR frequencies for the free ligands and their complexes together with our proposed assignments. The IR spectra of the complexes except Zn(SGA) and Co(SGA) and the free ligands, exhibit a strong and broad band in the region 3370-3421 cm^{-1}, which can be attributed to the stretching vibration of the water groups(13). The C=N imine stretching vibration is observed in the region 1653-1655 cm^{-1} for the free ligands, clearly indicating the formation of Schiff bases. When the spectra of the complexes are compared with those of the free Schiff base ligands, the ν(C=N) band is shifted to a lower frequency, indicating that the imino nitrogen is coordinated to the metal ion. The negative shift of the band indicates weakening of the C-N link(14).

In the spectra of complexes, the asymmetric carboxyl stretching and symmetric carboxyl stretching absorption bands are shifted to a higher frequency, indicating the formation of a linkage between a metal ion and a carboxylate oxygen(15, 16) . The asymmetric and symmetric carboxyl stretching absorption bands observed for the complexes are close to 1600 and 1400 cm^{-1}, affording $\Delta\nu$ (ν_{as} -ν_s) values in the region 185-210 cm^{-1}, which is characteristic of a monodentate(17).

The characteristic absorption bands appear in the regions 1223 and 1536 cm^{-1}. These can be assigned to phenolic C-O and amide N-H stretching vibrations for the free ligand,

Table II. Thermoanalytical data

Compound	DTG peak	Percent weight loss Found (calcd.)%	Probable composition of expelled group
Cu(SGA). $2H_2O$	97	10.52 (10.36)	2 H_2O
Ni(SGA).$4H_2O$	86	19.35 (19.02)	4 H_2O
Cu(SGP). H_2O	92	4.81 (4.44)	H_2O
Zn(SGP).H_2O	103	4.65 (4.42)	H_2O
Ni(SGP).$2H_2O$	78	9.01 (8.60)	2 H_2O
Co(SGP).$2H_2O$	96	8.93 (8.60)	2 H_2O

Table III. Infrared spectral data (cm^{-1})

Compound	ν(OH)	ν(C=N)	νas(COO)	νs(COO)	ν(CONH)	ν(C-O)
KH(SGA).H_2O	3370	1655	1589	1401	1532	1245
Cu(SGA).$2H_2O$	3411	1639	1598	1399	1540	1286
Zn(SGA)	---	1647	1611	1404	1548	1286
Ni(SGA). $4H_2O$	3386	1631	1598	1405	1539	1278
Co(SGA)	---	1639	1606	1409	1540	1267
KH(SGP).H_2O	3394	1653	1588	1393	1524	1268
Cu(SGP).H_2O	3402	1634	1598	1401	1542	1284
Zn(SGP).H_2O	3419	1639	1597	1410	1548	1286
Ni(SGP). $2H_2O$	3421	1631	1594	1409	1540	1284
Co(SGP).$2H_2O$	3411	1639	1598	1397	1548	1278

Table IV. Electronic spectral data (in methanol, 10^{-3}M, lg ε)

Compound	π-π* (benzene ring/COO)		π-π* (C=N)	d-d
$KH(SGA). H_2O$	207 (4.01)	274 (3.45)	310 (3.03)	
$Cu(SGA). 2H_2O$	204 (3.95)	220 (4.01)	368(3.42)	641(1.93)
	238 (3.96)	268 (3.77)		
Zn(SGA)	201 (3.61)	221 (3.71)	362(3.26)	
	268 (3.45)	236(3.69)		
$Ni(SGA).4H_2O$	204 (3.79)	234 (3.90)	328 (3.17)	
Co(SGA)	226 (4.17)	247 (4.16)	330 (3.53)	
$KH(SGP). H_2O$	225 (3.91)	254 (3.91)	316 (3.51)	
$Cu(SGP).H_2O$	218 (3.53)	238 (3.48)	368 (3.23)	610 (1.85)
	268(3.29)			
$Zn(SGP).H_2O$	216 (3.45)	237 (3.36)	364 (3.06)	
	269 (3.17)			
$Ni(SGP).2H_2O$	228 (3.90)		362 (3.24)	
$Co(SGP).2H_2O$	238 (4.24)		364 (3.44)	

respectively. The phenolic stretching C-O and amide N-H stretching are shifted to a higher frequency, implying that the phenolic oxygen and amide nitrogen atom on the peptide chain form a coordination complex to the metal ion(16, 18, 19). In the far IR spectra of all the complexes, conclusive evidence regarding the bonding of nitrogen and oxygen is provided by the occurrence of bands at 587-515 (M-N) and 507-424 cm^{-1} (M-O)(17).

Electronic spectra

The electronic spectral data of the synthesized compounds in the methanol solutions are given in Table IV. The spectra of two free Schiff bases exhibit three absorption bands in

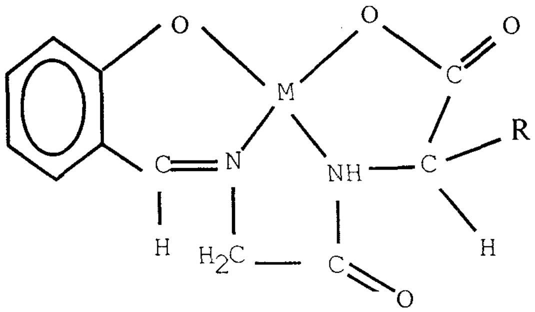

Fig. 2. Suggested structure of complexes
M = Cu(II), Zn(II), Ni(II) and Co(II)
R = CH_3, SGA; R = CH_2Ph, SGP

the regions 207-225, 254-274, and 310-316 nm. These bands are attributed to π-π* transitions(2,10), the first and second with those of the benzene ring and the COO group, and the third with those of the imino group. In the complexes, the imino π-π* transition is shifted to a longer wavelength as a consequence of coordination when binding with the metal, confirming the formation of the Schiff base metal complexes(2).

Conclusion

On the basis of the analytical data which afford the general formula M(SGA).nH_2O and M(SGP).nH_2O, and the IR and UV features obtained for the complexes, we can deduce that the dipeptide Schiff base ligands are coordinated to the central metal as tetradentate O-N-N-O ligands where two five-chelated rings and one six-chelated ring are formed. The bonding sites are the carboxylate oxygen, imino nitrogen, amide nitrogen and phenolic oxygen. We assume a similar structure for the complexes in Fig. 2.

Acknowledgment

This work was supported by the key Discipline Fund of Tianjin Bureau of Higher Education.

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Date Received: March 31, 1999
Date Accepted: April 25, 1999