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Synthesis and Properties of Zn(II)-Salicylidene Amino Acid Complexes

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The synthesis of nine Zn(II) salicylideneamino acid complexes is reported. The structures of the complexes have been investigated by chemical analyses, electronic and infrared spectra, as well as molar conductance measurements. The apparent complex formation constants have been determined.

(Keywords: Complexes; Molar conductance; UV; IR)

Synthese und Eigenschaften von Zn(II)-*Salicyliden-Aminosäure-Komplexen*

Es wird die Synthese von neun Zn(II)-Salicylidenaminosäurekomplexen berichtet. Die Struktur der Komplexe wurde mittels chemischer Analyse, den Elektronen- und IR-Spektren und auch aus Leitfähigkeitsmessungen ermittelt. Die effektiven Komplexbildungskonstanten wurden ebenfalls bestimmt.

Introduction

Although metal complexes of *Schiff* bases derived from *o*-hydroxyaromatic aldehydes and various amines have been the subject of intensive research, the chelates in which amino groups are provided by amino acids have received comparatively little attention in literature [1–6]. These latter chelates were proved to be of great importance in elucidating the mechanism of transamination [7, 8] reactions. In continuation of our studies on the synthesis and structure of new UO_2(II), Th(IV), Ce(III) and In(III) complexes of salicylideneamino acids [9, 10], this paper describes the synthesis, properties and chemical structure of Zn(II) complexes of various salicylideneamino acids.

Experimental

All chemicals employed were of A.R. products. The amino acids used in this investigation are glycine, *DL*-alanine, *L*-valine, *L*-leucine, *DL*-isoleucine, *L*-serine, *L*-aspartic acid and *L*-glutamic acid. A stock solution ($2.5 \cdot 10^{-2}$ *M*) of zinc salt, $Zn(NO_3)_2 \cdot 6\,H_2O$, was prepared by dissolving the calculated amount in the proper volume of absolute ethanolic solution and standardized gravimetrically. $5 \cdot 10^{-2}$ *M* of each amino acid was prepared by dissolving the accurately weighed amount in an appropriate volume of water-ethanol solution mixture (1 : 1). Lower molarity solutions were prepared by dilution.

The solid Zn(II) salicylideneamino acid complexes were synthesized making use of the following general method: A solution mixture of $Zn(NO_3)_2 \cdot 6\,H_2O$ in ethanol, amino acid in water and salicylaldehyde in ethanol was prepared in the molar ratios 1 : 1 : 1, as well as 1 : 2 : 2. The mixture was then refluxed for two hours on a water both. The solid Zn(II) complexes of salicylidene-glycine and *DL*-alanine were obtained by concentration and cooling of the reaction mixtures where orange and yellow crystals were formed respectively. The Zn(II) complexes of the other salicylideneamino acids used in this study were separated during reflux. The solid products were finally filtered off, washed with water, ethanol 95%, ethyl ether and dried. The physical properties, together with the results of the chemical analyses of these complexes are listed in Table 1. The complexes of Zn(II)-salicylideneaspartic and -glutamic acids were hygroscopic.

The electrolytic conductance measurements were carried out at 25 °C in absolute ethanol or *DMF* using a Pye conductance bridge. The UV and visible electronic spectra were recorded on a Pye Unicam SP 100 spectrophotometer using matched 1 cm^3 stoppered silica cells. The IR spectra of the complexes were performed in potassium bromide using a Beckman 20 Infrared Spectrophotometer.

Results and Discussions

Electronic Spectra and Stoichiometry of Complexes

The formation of Zn(II) salicylideneamino acid complexes was inferred by the appearance of a characteristic new absorption band in the wavelength range 365–375 nm for the Zn(II), salicylaldehyde, and amino acid ternary component solutions (each component $\geqslant 5 \cdot 10^{-3}$ *M*). In most cases maximum complex formation was achieved after two hours, where more or less constant absorbance values were obtained (c.f. Fig. 1).

The visible absorption band observed in the recorded electronic spectra of the ternary component solutions can be assigned to an intramolecular charge transfer interaction taking place within the complexed salicylideneamino acid moiety. However, such type of interaction is activated by the presence of the coordinated Zn(II) as represented schematically (see below).

Due to poor solubility of both aspartic and glutamic acids in ethanol, no spectral data were reported for their ternary complex solutions.

The stoichiometries of the different Zn(II)-salicylideneamino acid complexes formed in solution from the reaction of Zn(II) with the two

Table 1. *Chemical analyses, colour, decomposition temperatures and molar conductance values (ohm^{-1} cm^2 mol^{-1}) for* Zn(II)-*salicylidene amino acid complexes*

Complex	Formula	Colour	Decomposition Temp. °C	Molar conductance	Calc.%		Found %	
					C	N	C	N
Zn(II)-sal-gly.	$[(C_9O_3NH_8)_2Zn(H_2O)]H_2$	orange	166	[a]	49.16	6.37	49.04	6.18
Zn(II)-sal-alan.	$[(C_{10}O_3NH_9)_2Zn(H_2O)]H_2$	dark brown	>300	[a]	51.35	5.99	51.22	5.85
Zn(II)-sal-val.	$[(C_{12}O_3NH_{13}Zn(H_2O)]$	yellow	238	6.28[b]	47.62	4.63	47.52	4.43
Zn(II)-sal-leuc.	$[(C_{13}O_3NH_{15})Zn(H_2O)]$	pale grey	>300	10.60[b]	49.31	4.42	49.52	4.24
Zn(II)-sal.-isoleuc.	$[(C_{13}O_3NH_{15})Zn(H_2O)]$	black	>300	[a]	49.31	4.42	49.22	4.52
Zn(II)-sal.-norleuc.	$[(C_{13}O_3NH_{15})Zn(H_2O)]H_2$	yellow	280	[a]	49.31	4.42	49.12	4.29
Zn(II)-sal.-ser.	$[(C_{10}O_4NH_9)Zn(H_2O)]$	pale yellow	84	[a]	41.33	4.82	41.13	4.62

[a] Not enough soluble in ethanol or *DMF*
[b] Measured in *DMF*

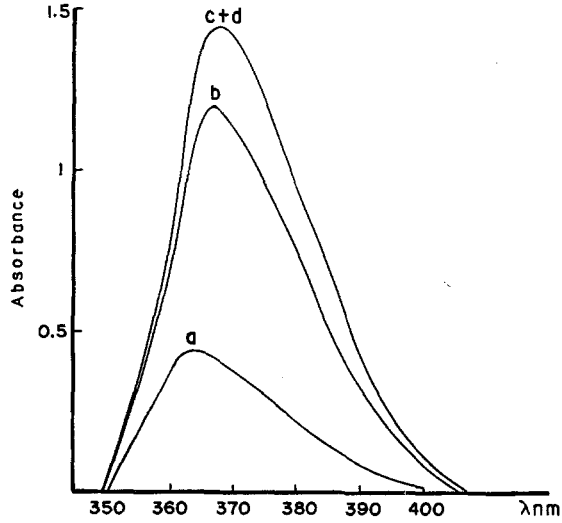


Fig. 1. Electronic absorption spectra of the ternary components solution Zn(II)-salicylaldehyde-*DL*-Alanine, each $5 \cdot 10^{-3}$ *M*. *a* After 5 minutes; *b* after 15 minutes; *c* after 120 minutes; *d* after 180 minutes [blank is a solution mixture of $5 \cdot 10^{-3}$ *M* of both Zn(II) and salicylaldehyde]

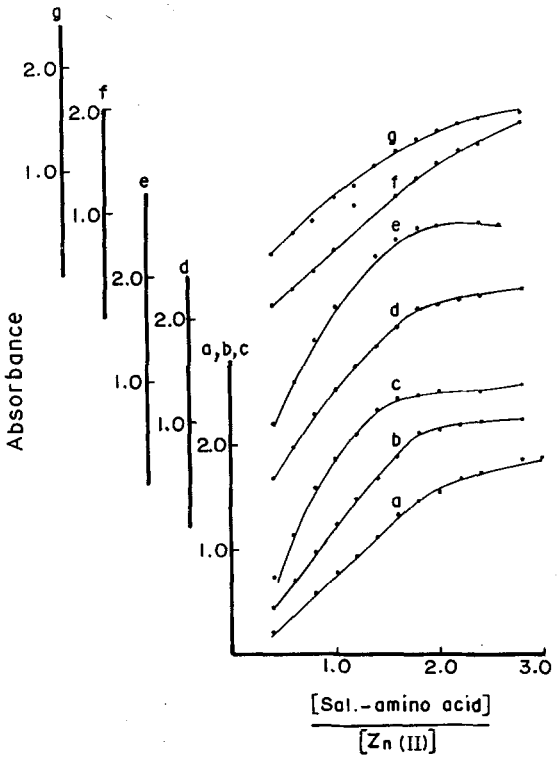


Fig. 2. Molar ratio method plots for the different Zn(II)-salicylideneamino acid complexes. *a* Gly ($\lambda = 375$ nm); *b* *DL*-Alan. ($\lambda = 380$ nm); *c* *L*-Valine ($\lambda = 350$ nm); *d* *L*-Leuc. ($\lambda = 350$ nm); *e* *DL*-Isoleuc. ($\lambda = 350$ nm); *f* *DL*-Norleuc. ($\lambda = 370$ nm); *g* *L*-Ser. ($\lambda = 370$ nm)

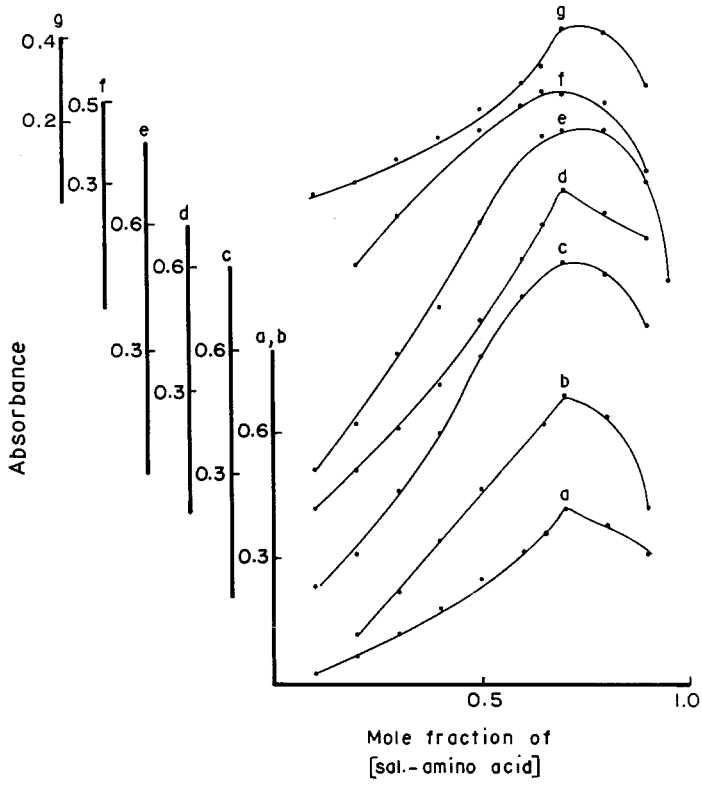


Fig. 3. *Job* method plots for the different Zn(II)-salicylidene amino acid complexes. *a* Gly ($\lambda = 370$ nm); *b* *DL*-Alan. ($\lambda = 370$ nm); *c* *L*-Valine ($\lambda = 350$ nm); *d* *L*-Leuc. ($\lambda = 350$ nm); *e* *DL*-Isoleuc. ($\lambda = 350$ nm); *f* *DL*-Norleuc. ($\lambda = 350$ nm); *g* *L*-Ser. ($\lambda = 370$ nm)

components (salicylaldehyde and amino acid) were determined using the conventional spectrophotometric molar ratio and continuous variation methods [11, 12]. Figures 2 and 3 reveal the possible formation of a ternary chelate in solution from the three components with a stoichiometric ratio 1 : 2 : 2 [Zn(II): salicylaldehyde : amino acid].

Apparent Formation Constants

The apparent formation constant values (K_f) of the different 1 : 2 : 2 Zn(II)-salicylideneamino acid complexes formed in solution were calculated from the results of the spectrophotometric continuous variation method. The following equation was applied [13]:

$$K_f = \frac{A/A_m}{4(1 - A/A_m)^3 C^2}$$

where A_m is the limiting absorbance corresponding to the maximum formation of the complex and A is the absorbance at a given metal ion concentration C.

Careful examination of the K_f values listed in Table 2 suggests that the stability of the ternary complex decreases with the increase in size of the amino acid side chain. This is due to the expected increase in steric interaction through the ternary complex in the same direction. A similar observation was reported before by *Schideggar* [14] for the Zn(II) *Schiff* base complexes *o*-oxoglutarate and pyruvate with α-alaninate and glutamate.

Structure of the Complexes

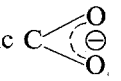
Assignments of the important significant infrared bands of the synthesized Zn(II)-salicylideneamino acid solid complexes are given in Table 3. The broad absorption band located at 3 200–3 500 cm^{-1} can be

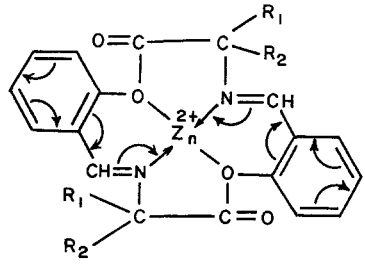
Table 2. *Apparent formation constants (K_f) for the* Zn(II)*-salicylidene amino acid complexes*

Salicylidene-amino acid	K_f
Sal.-gly.	$2.79 \cdot 10^9$
Sal.-alan.	$6.60 \cdot 10^8$
Sal.-val.	$3.31 \cdot 10^8$
Sal.-leuc.	$2.45 \cdot 10^8$
Sal.-isoleuc.	$1.82 \cdot 10^8$
Sal.-norleuc.	$2.53 \cdot 10^8$
Sal.-ser.	$2.45 \cdot 10^8$

Table 3. *Assignment of the significant infrared bands of the* Zn(II) *salicylidene amino acid complexes*

Sal.-gly.	Sal.-alan.	Sal.-val.	Sal.-leuc.	Sal.-isoleuc.	Sal.-norleuc.	Sal.-ser.	Assignment
3 400	3 500	3 320	3 200	3 300	3 400	3 400	O—H stretching
1 660	1 618	1 645	1 645	1 620	1 610	1 650	C=N stretching
1 600	1 530	1 615	1 600	1 575	1 555		
1 435	1 460	1 450	1 475	1 530	1 520	1 595	C=C stretching
1 415	1 440		1 450	1 445	1 435		
1 400	1 408	1 385	1 380	1 372	1 400	1 400	 sym. stretching
1 300	1 320	1 310	1 280	1 300	1 310	1 310	Phenolic C—O stretching

attributed to the stretching vibration of the OH group. This agrees with the results of analysis (Table 1), showing that water molecules are present. The centered band appearing in the IR spectra of the solid complexes in the region 1 660–1 610 cm^{-1} could be attributed to the azomethine stretching vibration. The two bands displayed in the regions 1 408–1 372 and 1 320–1 280 cm^{-1} can be ascribed to the symmetric  and phenolic C—O stretchings respectively [15–17]. Each of these three bands exhibits marked blue shift in its frequency compared to the free ones [15–17]. This suggests that the three bonding sites, the nitrogen of the azomethine and the two oxygen atoms of carboxylate and salicylaldehyde moiety, have been involved in complex formation where two, five and six membered chelated ring are formed. The salicylideneamino acid coordinates to Zn(II) as bivalent anion tridentate ligand. The observed shift to higher frequency values in the $\nu_{C=N}$, $\nu_{sym.\ COO^-}$ and $\nu_{Ph\text{-}CO}$ vibrations is presumably due to the high mesomeric interaction in the six-membered chelated ring as shown in the schematically represented complex structure.



It should be noted that the absorption band due to the antisymmetric stretching vibration of sym. COO^- (1 500–1 650 cm^{-1}) [15] is expected to be obscured by the high intensity bands of the C=C stretching vibrations observed at 1 415–1 595 cm^{-1} [18] as well as by the strong C=N stretching band.

The observed low values of the molar conductance of the 1 : 1 : 1 Zn(II) salicylidenevaline and Zn(II) salicylideneleucine complexes in *DMF* (Table 1) suggest the nonelectrolyte behaviour of such chelates [19].

According to the foregoing discussion together with the results of chemical analysis of the synthesized complexes, the structure of the 1 : 2 : 2 Zn^{2+} : salicylideneamino acid complex can be represented schematically as follows:

$R_1 = H$

$R_2 = H$ (glycine); CH_3 (*DL*-alanine); $(CH_3)_2CH$ (*L*-valine); CH_3CHCH_2 (*L*-leucine); CH_3CH_2CH (*DL*-isoleucine); $CH_3(CH_2)_3$ (*DL*-norleucine); HO (*L*-serine).

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