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Research Article

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One-step solid-solid synthesis, characterization and thermal decomposition of zinc(II) complexes of vanillin Schiff base ligands

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ABSTRACT

The zinc(II) complexes of taurine-vanillin and alanine-vanillin Schiff base were synthesized with taurine or L-alanine, and vanillin, zinc acetate and potassium hydroxide as main raw materials by one-step solid-solid reaction at room temperature. The composition and structure of the complexes were characterized by elemental analyses, molar conductance, Fourier transform infrared spectra (FTIR), X-ray powder diffraction (XRD), and thermogravimetry and differential scanning calorimetry (TG-DSC). The composition of complexes is $[Zn(tau\text{-}van)(H_2O)]\cdot 0.5H_2O$ *and* $[Zn(ala\text{-}van)(H_2O)]\cdot 0.5H_2O$*, and it is non-electrolytic nature. The experimental results indicate that the zinc ions are all four-coordinated by imino nitrogen, carboxylic oxygen or sulfonic oxygen and phenolic oxygen atoms from the Schiff base ligands, and oxygen atom from coordinated water molecule, respectively. The thermal decomposition processes of the zinc(II) complexes under air include dehydration and pyrolysis of the ligands, and the final residue is zinc oxide.*

Key words: zinc(II) complex; vanillin Schiff base; taurine; *L*-alanine; room temperature solid-solid synthesis; thermal decomposition

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INTRODUCTION

A huge interest on the complexes of Schiff bases derived from amino acids and salicylaldehyde has emerged due to their structural, magnetic and electrochemical properties, as well as their potential use as models for a number of important biological systems. Synthetic vanillin is used as a flavoring agent in foods, beverages and pharmaceuticals. However, only few transition metal complexes of vanillin were reported. The Schiff base complexes of transition-metal ions have been extended enormously and embraced wide and diversified subjects comprising vast areas of organometallic compounds and various aspects of biocoordination chemistry [1-5]. Schiff bases and their complexes have been found to posses the pharmacological activities, such as antibacterial [6-9], antifungal [9, 10], antitumor [11], antimalarial [12], anticonvulsant [13], and antiviral agents [14]. Studying Schiff bases of amino acids and their complexes have important significance to bioinorganic chemistry and medicine field. The use of Schiff bases as ligands in the formation of transition-metal complexes had been extensively studied, but the Schiff base ligands and its complexes were previously synthesized in some solvent, and most synthetic method was performed in ethanol or methanol solution [15–23]. This method had the disadvantages of long response time, the use of a large amount of solvents, environmental pollution, and low yield. Solid-solid chemical reaction at room temperature is a wide kind of methods for the preparation of some compounds, and the method has a high yield rate and selectivity [24, 25].

Amino acids and their compounds with different metal ions play an important role in pharmaceutical industries. Taurine, or 2-aminoethanesulfonic acid, is very important non-natural amino acids in organism. Taurine is essential for cardiovascular function, and development and function of skeletal muscle, the retina and the central nervous system, and it also acts as an antioxidant and protects against toxicity of various substances (such as lead and cadmium) [26]. The complexes of taurine were used in many fields such as medicine and biochemistry. The complexes of the amino acid Schiff base synthesized by the one-step solid-solid reaction at room temperature have not been previously reported in literatures [27]. Based on the concept of green chemistry, in this work we have synthesized the zinc(II) complexes of the taurine-vanillin and alanine-vanillin Schiff base ligands, and studied their crystal structure, infrared spectra and thermal decomposition process.

EXPERIMENTAL SECTION

Materials and physical measurements

In addition to taurine and *L*-alanine were biochemical reagents, other chemical reagents used in the experiments were analytical grade as received from commercial sources with no further purification. Vanillin (3-methoxy-4-hydroxybenzaldehyde), taurine and *L*-alanine were purchased from Sinopharm Chemical Reagent Co., Ltd., and zinc acetate, potassium hydroxide and anhydrous ethanol were received from Chengdu Kelong Chemical Reagent Company.

The contents of carbon, hydrogen, nitrogen, sulfur and oxygen in the complexes were obtained by an Elementar Vario EL CUBE elemental analyzer. Zinc was determined by EDTA complexometric titration. Electrical conductivity was measured at 25 °C by a DDS-11A conductometer. The X-ray powder diffraction patterns of the complexes were recorded by a Rigaku D/Max-RB X-ray diffractometer, Cu K_α radiation at room temperature (λ = 0.154056 nm, step width: 2θ = 0.2°, scan speed: 8 °/min). The infrared spectra of the complexes were measured by a Nicolet 5700 Fourier transform infrared spectrometer using potassium bromide pellets in the region 4000–400 cm^{-1}. Thermal analyses of the complexes were performed by a TA Q500 thermal analyzer, and the heating rate was suitably controlled at 10 °C min^{-1} under air atmosphere and the mass loss was measured from ambient temperature up to 600 °C.

Synthesis of the title complexes

Taurine (0.63 g, 5 mmol) and potassium hydroxide (0.28 g, 5 mmol) were weighed and placed in an agate mortar, and continually grinded until they became sticky. Then, vanillin (0.76 g, 5 mmol) was added and grinded continuously, the color of the reactants turned into yellow quickly, and the loose yellow powder solid was obtained after about 30 minutes. Afterwards zinc acetate dihydrate (1.10 g, 5 mmol) was added to the agate mortar, grinded continuously about 30 minutes. The reaction was carried out at room temperature. The resultant was washed repeatedly with distilled water and a little anhydrous ethanol. Lastly, the resultant was filtered and dried about 24 h in vacuum drying oven at 40 °C. The zinc complex of the taurine-vanillin Schiff base was pale-yellow powder, and the yield was about 85%. The zinc complex of the alanine-vanillin Schiff base was also synthesized by the similar method, and the product was pale-yellow powder and the yield was about 91%.

RESULTS AND DISCUSSION

The composition and properties of the complexes

The results of elemental analyses of the complexes are listed in Table 1. The composition formulae of the complexes are $ZnC_{10}H_{14}O_{6.5}NS$ (M_r = 349.68) and $ZnC_{11}H_{13}O_{4.5}N$ (M_r = 313.63), respectively. The calculated results of mass fraction of each element in the complexes are very close to the measured ones. Therefore, combined with the results of the infrared spectra and the thermal analysis, the possible molecular formulae of the complexes are $Zn(tau\text{-}van)\cdot 1.5H_2O$ and $Zn(ala\text{-}van)\cdot 1.5H_2O$, or $Zn[OC_6H_3(OCH_3)CH{=}NCH_2CH_2SO_2O]\cdot 1.5H_2O$ and $Zn[OC_6H_3(OCH_3)CH{=}NCH(CH_3)CH_2COO]\cdot 1.5H_2O$. The molar ratio of the Schiff base ligands to zinc(II) ion of the complexes is 1:1. The complexes are all stable at room temperature, non-hygroscopic, and partially soluble in water and ethanol. The molar conductance values of 10^{-3} mol/L DMF solutions of the complexes are in the range of 5–8 $S\cdot cm^2/mol$, the results indicate that the complexes are non-electrolytic nature.

Table 1 Elemental analyses results of the complexes (Calculated values are in brackets)

Complex	Formula	*w*(Zn)(%)	*w*(C)(%)	*w*(H)(%)	*w*(N)(%)	*w*(S)(%)	*w*(O)(%)
$Zn(tau\text{-}van)\cdot 1.5H_2O$	$ZnC_{10}H_{14}O_{6.5}NS$	18.83(18.70)	34.16(34.35)	4.15(4.04)	4.06(4.01)	9.25(9.17)	29.58(29.74)
$Zn(ala\text{-}van)\cdot 1.5H_2O$	$ZnC_{11}H_{14}O_{5.5}N$	20.83(20.85)	41.92(42.12)	4.35(4.50)	4.38(4.47)	–	28.18(28.06)

Analysis of X-ray powder diffraction

The X-ray powder diffraction patterns of the complexes are shown in Fig. 1. Compared with the raw materials, the strong peak locations of the resultants are changed obviously. The main strong peaks, which come from the reactants of taurine, *L*-alanine, vanillin and zinc acetate, are disappeared in X-ray powder diffraction patterns of the complexes. The diffraction angle (2θ), spacing (d) and diffractive intensity of the products are different from the reactive materials, which may explain that the above two products are not simple mixing of the reactants, but the formation of new compounds. At the same time, the new strong peaks show the new compounds formation rather than the mixture of the reactants. There is the small background, and the high and intense of diffraction peaks in the XRD patterns of the complexes, which indicate that the complexes have fine crystalline state.

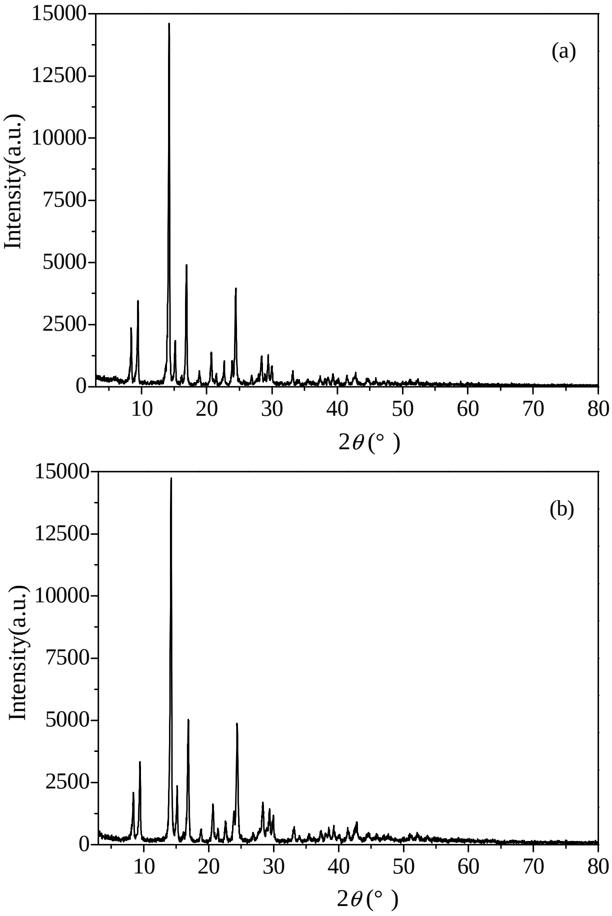

Fig. 1 X-ray powder diffraction patterns of the complexes Zn(tau-van)·1.5H_2O (a) and Zn(ala-van)·1.5H_2O (b)

FTIR spectra

The infrared spectra of the complexes are shown in Fig. 2. The absorption peaks from the stretching vibration of the bonds in the water molecule are in the region 3550–3200 cm^{-1} [28]. As Fig. 2 shows, there are some strong peaks in the range of 3550–3200 cm^{-1} in the infrared spectra of the complexes. This indicates that there are water molecules in the crystals of the complexes. Therefore, the infrared spectra demonstrate the existence of the coordination water or lattice water molecules in the complexes, and support the molecular formulae of the complexes.

Fig. 2(a) shows, the infrared spectrum of Zn(tau-van)·1.5H_2O makes out broad peaks at 3427 cm^{-1} and 3232 cm^{-1} due to the ν(O–H) band in water molecule. The absorption peaks at 927 cm^{-1} and 726 cm^{-1} are assigned to the rocking and wagging vibrations of the hydroxyl, and which indicate that there is the coordinated water molecule in the complexes [20]. This is in accord with the result of thermal analysis. The characteristic absorption peak at 1645 cm^{-1} can be assigned to the absorption peak of the ν(C=N) stretching vibration [8]. The absorption peaks at 1340 cm^{-1} and 1114 cm^{-1} can be assigned to the absorption peaks of the ν_{as}(S=O) and ν_{s}(S=O) stretching vibration, and the absorption peaks at 781 cm^{-1} and 635 cm^{-1} arise from ν_{as}(S–O) and ν_{s}(S–O) stretching vibration, respectively. Compared with the characteristic peaks of sulfonic group, the peaks shift obviously, this shows that the sulfonic group involves in coordination. The absorption peak at 1283 cm^{-1} is assigned to the phenolic ν(ph–O) stretching vibration. Compared with the ligand, the peak in the complex shifts obviously towards low-frequency region, and this indicates that the phenolic oxygen is coordinated with Zn^{2+} ion. In the low-frequency region, the absorption peak at 594 cm^{-1} is assigned to the stretching vibration of the Zn−N bond, and the absorption peaks at 466 cm^{-1} and 430 cm^{-1} arise from the stretching vibration of the Zn−O bond [28].

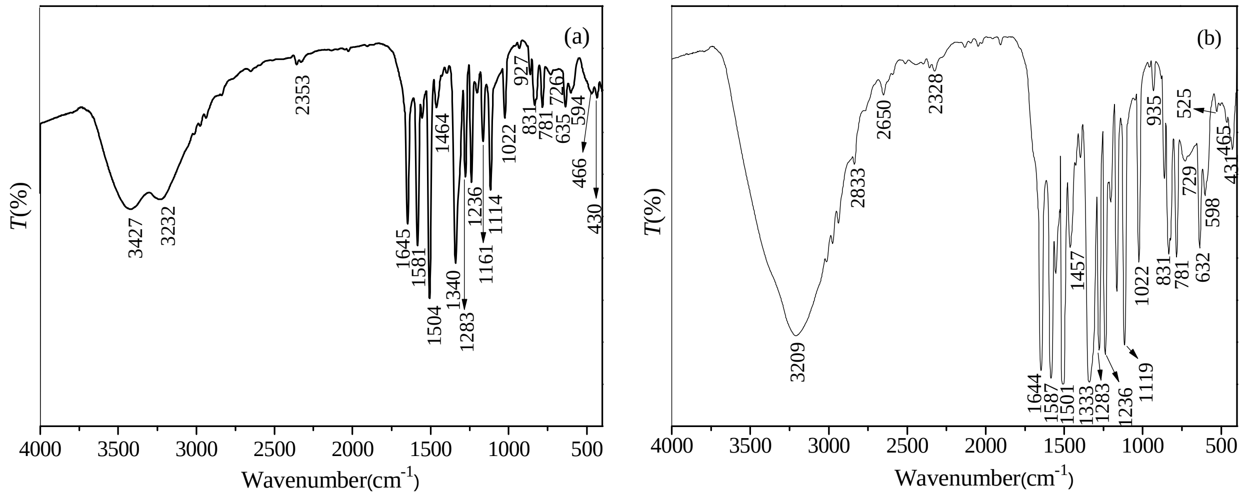

Fig. 2 Infrared spectra of the complexes Zn(tau-van)·1.5H_2O (a) and Zn(ala-van)·1.5H_2O (b)

Why are the vibration frequencies of the two Zn–O bonds different? The frequency of stretching vibration of a chemical bond A–B is related to the mass of the A and B atom. The larger the mass of the A or B atom is, the lower the frequency of the stretching vibration of the A–B bond is. Besides, other atoms or groups bonded to the A or B atom can also affect the frequency of the stretching vibration of the A–B bond. For example, when the O atom bonds with the metal ion, an O atom is bonded to a group with a very large molecular mass, the 'apparent mass' of the O atom seems to become larger than the mass of an O atom alone. The mass of the –C_6H_3 group is much larger than that of –COO$^-$ group. Therefore, we can reasonably assume that the frequency of the stretching vibration of the Zn–O bond between the Zn^{2+} ion and the O atom of the –OC_6H_3 group must be lower than that of the Zn–O bond between the Zn^{2+} ion and the O atom of the –COO$^-$ carboxyl group [29].

Fig. 2(b) shows, a broad band at 3209 cm^{-1} in the infrared spectrum of Zn(ala-van)·1.5H_2O is assigned to the v(O–H) in water molecule, and the absorption peaks at 935 cm^{-1} and 729 cm^{-1} arise from the rocking and wagging vibrations of the coordinated water molecules. The absorption peak at the range of 1700–1740 cm^{-1} of carbonyl in the alanine-vanillin Schiff base ligand disappears in the complexes. The characteristic absorption peak at 1644 cm^{-1} can be assigned to the absorption peak of the v(C=N) stretching vibration. The absorption peaks at 1587 cm^{-1} and 1333 cm^{-1} can be assigned to the absorption peaks of the v_{as}(COO$^-$) and v_s(COO$^-$) stretching vibration, respectively. The difference value of 254 cm^{-1} between v_{as}(COO$^-$) and v_s(COO$^-$) is in line with a monodentate type of coordination [27]. The absorption peak at 1283 cm^{-1} arises from the v(ph–O) stretching vibration. The band at 598 cm^{-1} is assigned to the v(Zn−N) bond, and the peaks at 465 cm^{-1} and 431 cm^{-1} arise from the v(Zn–O) bond [28]. From the IR results, it may be concluded that the Schiff base ligand is tridentate and coordinates with the zinc ion through the azomethine nitrogen, phenolic oxygen and carboxylic oxygen atoms.

Thermal analysis

Studying the thermal decomposition process of various Schiff base complexes is helpful to the understanding of the coordination structure of the complexes [29–31]. The TG-DSC curves of the complexes from room temperature to 600 °C are shown in Fig. 3. The possible thermal decomposition processes, the experimental and calculated results for the thermal analysis of the complexes are summarized in Table 2.

Fig. 3(a) shows that there is one endothermic peak and two exothermic peaks in the DSC curve. The first, endothermic peak at 156 °C accompanies evidently mass loss, and the sample will gradually lose 1.5H_2O molecules. The experimental percentage mass loss (8.19%) closes to the calculated one (7.73%). This is consistent with the results of elemental analyses and infrared spectra of the zinc(II) complex. The coordinated water molecules should be eliminated at higher temperatures than the water molecules of hydration. The water molecule of coordination is usually eliminated in the temperature range 100–316 °C [32]. Because of the high temperature of loss water, the complex should be stored in a coordinated water molecule. The organic part of the complexes may decompose in one or more step with the possibility of the formation of one or two intermediates. These intermediates may finally decompose to stable metal oxides. Thereafter, sequential exothermic peaks at 334 °C and 414 °C correspond to step-by-step oxidation and decomposition of the ligand. The mass loss of 38.43% in TG curve corresponds to lose the groups of CH_3CN, –CH_2 and SO_3 (Calcd. mass loss, 38.64%), and the mass loss of 30.23% in TG curve corresponds to lose the group of –$CH_3OC_6H_3$ (Calcd. value, 30.35%). The complex is decomposed completely at about 560 °C. The final residue is zinc oxide, and the experimental result (23.15%) is in agreement with the calculated result (23.28%).

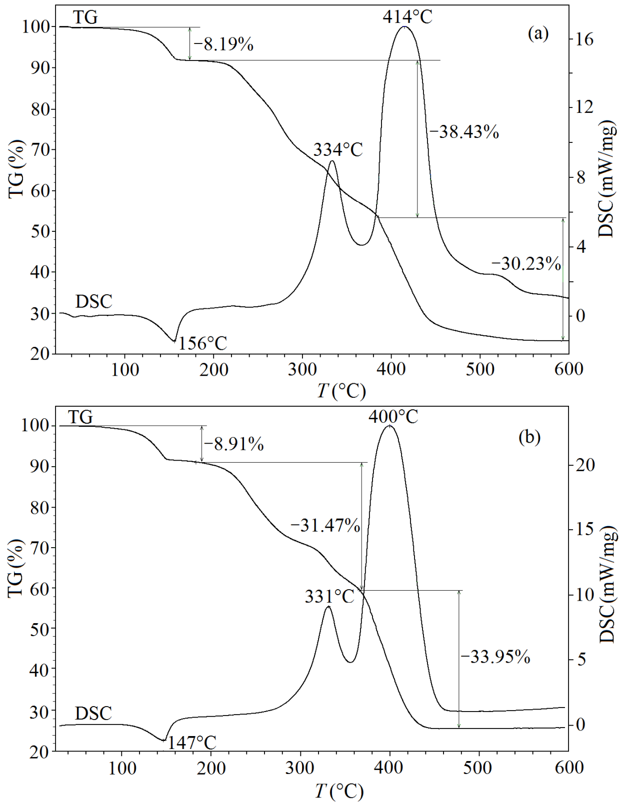

Fig. 3 TG-DSC curves of the complexes Zn(tau-van)·1.5H$_2$O (a) and Zn(ala-van)·1.5H$_2$O (b)

Table 2 Thermal decomposition data of the Schiff base complexes

Reaction	Peak Temp. in DSC (°C)	Mass loss (%)	
		$m_{\text{exp.}}$	$m_{\text{theor.}}$
Zn(tau-van)·1.5H$_2$O ↓ –1.5H$_2$O Zn[OC$_6$H$_3$(OCH$_3$)CH=NCH$_2$CH$_2$SO$_2$O]	156 (endo.)	8.19	7.73
↓ –CH$_3$CN, –CH$_2$, –SO$_3$ Zn[OC$_6$H$_3$(OCH$_3$)]	334 (exo.)	38.43	38.64
↓ –CH$_3$OC$_6$H$_3$ ZnO	414 (exo.)	30.23 23.15^a	30.35 23.28^b
Zn(ala-van)·1.5H$_2$O ↓ –1.5H$_2$O Zn[OC$_6$H$_3$(OCH$_3$)CH=NCH(CH$_3$)COO]	147 (endo.)	8.91	8.62
↓–CH$_3$CN, –CH$_2$, –CO$_2$ Zn[OC$_6$H$_3$(OCH$_3$)]	331 (endo.)	31.47	31.59
↓ –CH$_3$OC$_6$H$_3$ ZnO	400 (exo.)	33.95 25.67^a	33.84 25.95^b

[a] The experimental percentage mass of the residue in the sample, [b] the calculated percentage mass of the residue in the sample.

Fig. 3(b) shows that there is one obvious endothermic peak and two exothermic peaks in the DSC curve. The first, the endothermic peak at 147 °C accompanies 8.91% of mass loss from 1.5 water molecules (Calcd. value, 8.62%). Because of the high temperature of loss water, the water molecules should comprise one coordinated water molecule. Thereafter the exothermic peak at 331 °C accompanies 31.47% of mass loss, and it may lose the groups of CH$_3$CN, –CH$_2$ and CO$_2$ (Calcd. mass loss, 31.59%). Finally exothermic peak at 400 °C corresponds to entire oxidation and decomposition of the ligand and loss of –CH$_3$OC$_6$H$_3$ group, the experimental mass loss of 33.95% closes to the calculated value of 33.84%. The final remnant mass from TG curve is 25.67%, and it is in agreement with the calculated result (25.95%) of the residue zinc oxide.

CONCLUSION

Two zinc(II) complexes of tanrine-vanillin and alanine-vanillin Schiff base had been directly synthesized by one-step solid-solid reaction at room temperature. The complexes were characterized by elemental analyses, molar conductance, XRD, FTIR and TG-DSC. The two complexes have similar space structure, and the zinc(II) ions are all four-coordinated by imino nitrogen, carboxylic oxygen or sulfonic oxygen, and phenolic oxygen atoms from the Schiff base ligands, and oxygen atom from the coordinated water molecule, respectively. The possible molecular formulae of the complexes are $[Zn(tau\text{-}van)(H_2O)]\cdot 0.5H_2O$ and $[Zn(ala\text{-}van)(H_2O)]\cdot 0.5H_2O$. The thermal decomposition processes of the complexes include dehydration, and pyrolysis of the ligands, and the final residue is zinc oxide. The advantages of the one-step solid-solid synthetic method are simple and convenient operation, solvent-free, high yield, energy saving, and being environmental friendly, and it is in accordance with the requirements of green chemistry.

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