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ALANINE- AND TAURINE-SALICYLAL SCHIFF BASE COMPLEXES OF MAGNESIUM

Synthesis, characterization and thermal decomposition

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The complexes of α-alanine-salicylal Schiff base of magnesium (α-ASSM), β-alanine-salicylal Schiff base of magnesium (β-ASSM) and taurine-salicylal Schiff base of magnesium (TSSM) were synthesized. The formulae of the complexes are $Mg[OC_6H_4CHNCH(CH_3)COO]\cdot 2H_2O$, $Mg[OC_6H_4CHNCH_2CH_2COO]\cdot 2H_2O$ and $Mg[OC_6H_4CHNCH_2CH_2SO_3]\cdot 2H_2O$. The crystal structure belongs to orthorhombic system with the lattice parameters: a=1.6954 nm, b=2.0873 nm and c=2.3037 nm for the α-ASSM, to orthorhombic system with the lattice parameters: a=1.5586 nm, b=1.8510 nm and c=2.6240 nm for the β-ASSM, to monoclinic system with the lattice parameters: a=1.3232 nm, b=1.4960 nm, c=2.1543 nm and β=98.04° for the TSSM, respectively. The results of the thermal decomposition processes and infrared spectra of the complexes show that the complexes may possess different coordination structures.

Keywords: *alanine, crystal structure, infrared spectra, magnesium, salicylal, Schiff base, taurine, thermal decomposition*

Introduction

The Schiff base complex is a kind of important compound due to some special functions. Various Schiff base complexes have been synthesized and studied with their biological or antitumor activity [1–3]. Salicylal is often used to synthesize Schiff base complexes because of its special structure [4–6]. Amino acid is not only a kind of aminocarboxylic acid, but also a kind of important biological compound for the body. As amino acid, alanine has two different molecular structures, namely α-alanine $CH_3CH(NH_2)COOH$ and β-alanine $H_2NCH_2CH_2COOH$. With certain biological function, taurine has been used as chemical medicaments. The molecular structure of taurine $H_2NCH_2CH_2SO_3H$ is similar to that of β-alanine $H_2NCH_2CH_2COOH$. Zhang *et al.* [7–9] have synthesized the dimmer taurine Schiff base complex $[Ni(TSSB)(Phen)(H_2O)]\cdot 4H_2O$, $[Ni(Br_2TSSB)(Bipy)(H_2O)]\cdot 0.86C_2H_5OH$ and $[Mg(Br_2TSSB)(Phen)(H_2O)]\cdot H_2O$. Mg(II) *bis*(pendant arm) macrocyclic Schiff-base complexes have also been prepared [10]. To study the thermal decomposition process of various Schiff base complexes is helpful to the understanding of the coordination structure of the complexes [11–15].

In this paper, we synthesize the complexes of α-alanine-, β-alanine- and taurine-salicylal Schiff base of magnesium and study their crystal structure, infrared spectra and thermal decomposition process.

Experimental

Synthesis of the α-ASSM was as follows. Firstly, dissolve 3.053 g (34.3 mmol) α-alanine and 1.372 g (34.3 mmol) NaOH in a beaker with distilled water, and dissolve 4.029 g (34.3 mmol) salicylal in a beaker with dehydrated alcohol, respectively. The alcohol solution of salicylal was added slowly into the solution of alanine and NaOH by a drop-wise way. The solution was slowly yellowing. Secondly, dissolve 4.871 g (34.3 mmol) magnesium acetate with distilled water. Slowly add the solution of magnesium acetate to the above yellow solution and stir it. In this case, the yellow precipitate occurred in the solution. The solution was held for 30 min after stired for 2 h. Thirdly, the precipitate was separated from the solution by filtration and was washed thoroughly with the 1:1 mixture solution of alcohol and distilled water. Lastly, the precipitate was dried in a vacuum desiccator with phosphorus pentoxide for a week. The yield was about 53%. According to the procedure mentioned above, the β-ASSM and TSSM were synthesized. The yield of β-ASSM and TSSM was about 57 and 35.5%.

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The contents of carbon, hydrogen and nitrogen in the resultants were determined by Elementar Vario EL III elemental analyzer. Magnesium was determined by EDTA titration. The analytical results are listed in Table 1. The powder X-ray diffraction patterns of the resultants were recorded by Rigaku D/max 2550 VB/PC X-ray diffractometer, CuK_{α_1} radiation at room temperature. The index results of the powder X-ray diffraction patterns are shown in Tables 2–4, respectively. The infrared spectra of the complexes were measured by Nicolet 5D-FT Spectrometer, KBr plate. The infrared spectra are shown in Fig. 1. Thermal studies were performed by Perkin Elmer Pyris/Diamond Thermal Analyzer, in air, a heating rate of 10°C min^{-1}. The sample mass was 5.943, 2.800 and 3.102 mg for the α-ASSM, β-ASSM and TSSM respectively. TG and DTA curves of the complexes are shown in Fig. 2. The possible thermal decomposition processes, the experimental and calculated results for the thermal analysis are summarized in Table 5.

Results and discussion

As is shown in Table 1, the composition formulae of the resultants are $MgC_{10}H_{13}NO_5$, $MgC_{10}H_{13}NO_5$ and $MgC_9H_{13}NSO_6$, respectively. Therefore, the most

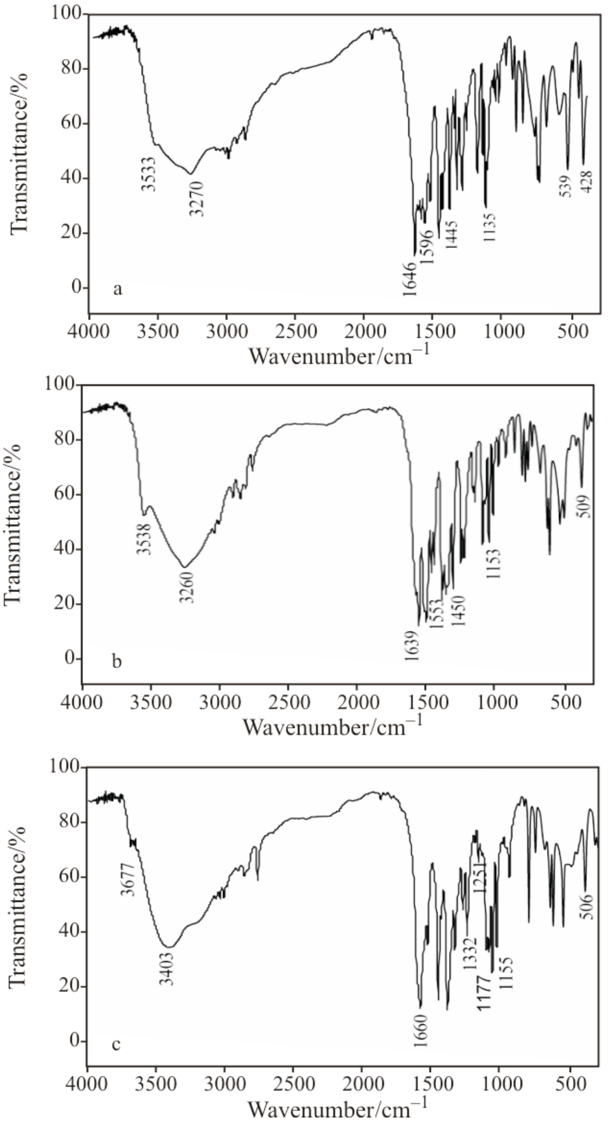

Fig. 1 Infrared spectra of the complexes of
a – α-alanine-salicylal Schiff base complex of magnesium, b – β-alanine-salicylal Schiff base complex of magnesium, c – taurine-salicylal Schiff base complex of magnesium

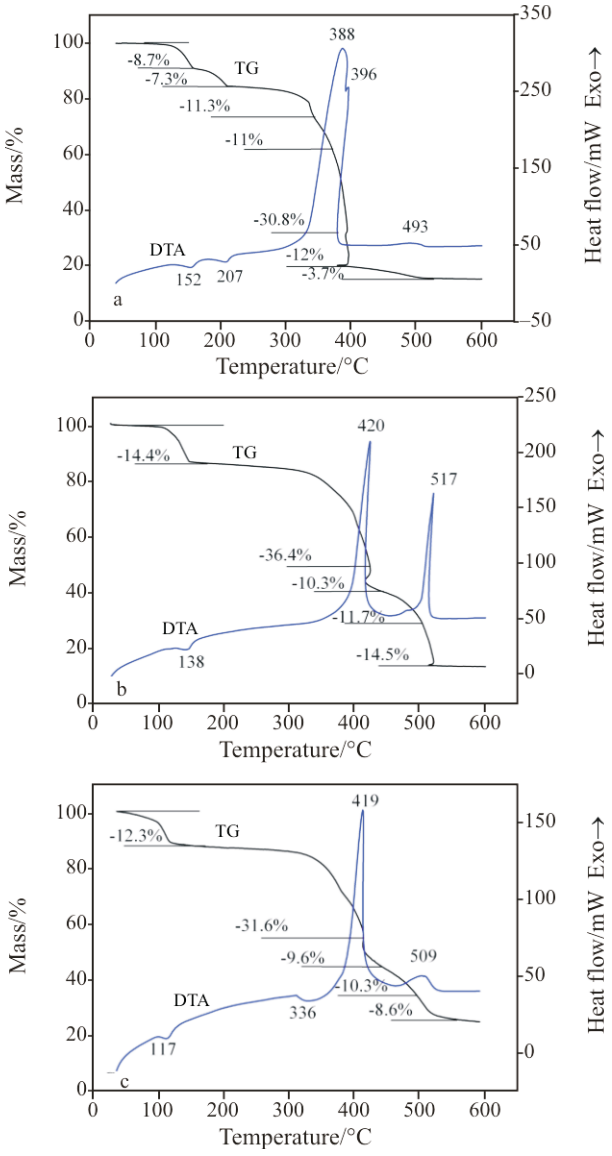

Fig. 2 TG and DTA curves of the complexes of
a – α-alanine-salicylal Schiff base complex of Mg,
b – β-alanine-salicylal Schiff base complex of Mg,
c – taurine-salicylal Schiff base complex of Mg

possible molecular formulae of the resultants will be $Mg[OC_6H_4CHNCH(CH_3)COO]\cdot 2H_2O$, $Mg[OC_6H_4CHNCH_2CH_2COO]\cdot 2H_2O$ and $Mg[OC_6H_4CHNCH_2CH_2SO_3]\cdot 2H_2O$. This indicates that the resultants may be the Schiff base complexes of magnesium.

The indexing to the powder X-ray diffraction patterns of the resultants shows that all the diffraction peaks in each pattern can be very readily indexed by a set of lattice parameters. As are shown in Tables 2–4, the largest relative deviation between the calculated and measured spacing is less than 0.5%. This demonstrates

Table 1 The results of the elemental analyses for the resultants

Composition formula	C/%	H/%	N/%	Mg/%
	Calculated (found)			
$MgC_{10}H_{13}NO_5$	47.75 (47.73)	5.21 (5.30)	5.57 (5.42)	9.67 (9.59)
$MgC_{10}H_{13}NO_5$	47.75 (47.20)	5.21 (5.72)	5.57 (5.23)	9.67 (9.62)
$MgC_9H_{13}NSO_6$	37.63 (38.30)	4.53 (4.31)	4.88 (4.58)	8.36 (8.62)

Table 2 The main experimental data and the calculated results for powder X-ray diffraction pattern of $Mg[OC_6H_4CHNCH(CH_3)COO]\cdot 2H_2O$ orthorhombic system: a=1.7560 nm, b=2.0850 nm, c=2.3036 nm

h k l	d_{exp}/nm	d_{cal}/nm	I/I_0	*h k l*	d_{exp}/nm	d_{cal}/nm	I/I_0
0 1 1	1.5438	1.5480	97	0 0 3	0.7702	0.7679	19
0 3 2	0.5965	0.5951	35	3 0 0	0.5855	0.5853	22
2 1 3	0.5583	0.5570	29	2 3 1	0.5311	0.5303	100
2 4 1	0.4414	0.4400	15	1 4 3	0.4195	0.4188	39
1 5 0	0.4059	0.4057	13	0 5 2	0.3921	0.3921	18
3 4 2	0.3681	0.3688	44	4 3 1	0.3648	0.3664	24
1 5 3	0.3590	0.3587	15	2 0 6	0.3512	0.3518	33
0 1 7	0.3245	0.3251	10	4 5 0	0.3029	0.3023	13
4 5 1	0.3002	0.2998	13	0 3 7	0.2976	0.2974	21
1 0 8	0.2840	0.2842	17	1 5 6	0.2784	0.2889	20
1 8 0	0.2579	0.2578	11	2 3 9	0.2311	0.2317	13
1 2 10	0.2236	0.2231	11	0 2 11	0.2049	0.2053	11
2 6 10	0.1874	0.1876	10				

Table 3 The main experimental data and the calculated results for powder X-ray diffraction pattern of $Mg[OC_6H_4CHNCH_2CH_2COO]\cdot 2H_2O$ orthorhombic system: a=1.5580 nm, b=1.8511 nm, c=2.6251 nm

h k l	d_{exp}/nm	d_{cal}/nm	I/I_0	*h k l*	d_{exp}/nm	d_{cal}/nm	I/I_0
1 0 0	1.5601	1.5580	20	0 0 2	1.3104	1.3125	87
0 2 0	0.9244	0.9255	100	0 2 3	0.6376	0.6359	20
2 1 3	0.5542	0.5551	14	2 0 6	0.3824	0.3815	15
2 4 3	0.3625	0.3622	11	2 3 6	0.3243	0.3245	12
2 3 8	0.2715	0.2715	14	1 7 3	0.2499	0.2499	12

Table 4 The main experimental data and the calculated results for powder X-ray diffraction pattern of $Mg[OC_6H_4CHNCH_2CH_2SO_3]\cdot 2H_2O$ monoclinic system: a=1.3232 nm, b=1.4960 nm, c=2.1543 nm, β=98.04°

h k l	d_{exp}/nm	d_{cal}/nm	I/I_0	*h k l*	d_{exp}/nm	d_{cal}/nm	I/I_0
0 2 1	0.7053	0.7059	100	0 3 1	0.4854	0.4856	30
2 2 1	0.4701	0.4695	61	1 4 1	0.3576	0.3569	80
1 5 2	0.2836	0.2836	10	0 5 4	0.2609	0.2609	10
0 1 9	0.2340	0.2341	10				

that the resultants are single phase. The crystal structure of α-ASSM $Mg[OC_6H_4CHNCH(CH_3)COO]\cdot 2H_2O$ and β-ASSM $Mg[OC_6H_4CHNCH_2CH_2COO]\cdot 2H_2O$ belongs to orthorhombic system, but, the crystal structure of TSSM $Mg[OC_6H_4CHNCH_2CH_2SO_3]\cdot 2H_2O$ belongs to monoclinic system. The molecular structure of β-alanine $H_2NCH_2CH_2COOH$ is different from that of α-alanine $CH_3CH(NH_2)COOH$ but similar to that of taurine $H_2NCH_2CH_2SO_3H$. Therefore, the molecular structure of the β-alanine-salicylal Schiff base is also different from that of the α-alanine-salicylal Schiff base but similar to that of the taurine-salicylal Schiff base. However, the crystal structures of the β-ASSM and the α-ASSM belong to orthorhombic system, while that of the TSSM belongs to monoclinic system. This shows the difference between the properties of alanine and taurine or the difference between the alanine-salicylal Schiff bases and taurine-salicylal Schiff base.

Generally, the absorption peaks from the stretching vibration of the O–H bonds in the water molecule are in the range of 3550–3200 cm^{-1} [16, 17]. As is shown in Fig. 1, 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 lattice water molecules in the complexes and support the molecular formulae of the complexes. We find that three infrared spectra are similar in the range of 1660 to 500 cm^{-1}. This means that there may be the same or similar groups in the complexes. For example, the characteristic absorption peak (ν=1650–1690 cm^{-1}) from the stretching vibration of the C=N bond in the Schiff base can be found at 1646, 1639 and 1660 cm^{-1} in Figs 1a–c, respectively. The strong absorption peak at 1135, 1153 and 1155 cm^{-1} in Figs 1a–c may be from the stretching vibration of the O=C bond in the OC_6H_4 group of the salicylal Schiff bases. The existence of these characteristic absorption peaks can demonstrate the formation of the Schiff base in the organic ligands. The characteristic absorption peaks from the symmetric and antisymmetric stretching vibration of the $-COO^{-1}$ group in the carboxylate are about at ν_s=1400 cm^{-1} and ν_{as}=1550–1610 cm^{-1} [16]. So, the peaks at 1445 and 1596 cm^{-1} in Fig. 1a and at 1450 and 1553 cm^{-1} in Fig. 1b can be assigned to the symmetric and antisymmetric stretching vibration of the $-COO^{-1}$ group in the α-alanine and β-alanine-salicylal Schiff base. The absorption peaks at 1332, 1251 and 1177 cm^{-1} in Fig. 1c may be from the various vibrations of the $-SO_3$ group in the taurine-salicylal Schiff base, because the three absorption peaks do not occur in the infrared spectra of the α-ASSM and β-ASSM. Generally speaking, the vibration frequency of the M–O bond in the carboxylate or sulfonate is below 600 cm^{-1}. There must be the Mg–O bond both in the α-ASSM, β-ASSM and TSSM. Hence, we assume that the strongest absorption peaks at 539, 509 and 506 cm^{-1} in the range of 500 to 600 cm^{-1} in Figs 1a–c are from the vibrations of the Mg–O bonds in the Schiff base complexes of magnesium. Meanwhile, we have also noted that Fig. 1a is different from Figs 1b and c in the range of 400 to 500 cm^{-1}. That is, there is a strong absorption peak at 428 cm^{-1} in Fig. 1a. We consider that this peak may be from the stretching vibration of the Mg–O bond between the Mg ion and O atom of the OC_6H_4 group in the α-ASSM. This conclusion can be supported by the thermal studies of the complexes.

As is shown in Fig. 2, the TG and DTA curves of the β-ASSM and TSSM are similar to each other, but, different from that of the α-ASSM. For example, as is shown in Table 5, the α-ASSM lose the first water molecule at 107°C, then, lose the second water molecule at 157°C. However, the two water molecules in the β-ASSM and TSSM lose at the same time. Besides, the dehydration temperature of the α-ASSM is slightly higher. The second mass loss of the α-ASSM is the elimination of the $-CH_3$ and –CH– groups from the α-alanine-salicylal Schiff base. Then, the ligand lose the –CH=N group. At 396°C, the ligand lose the $-C_6H_4$ group. Lastly, the residue loses CO_2. The pyrolytic product of the α-ASSM is MgO. However, after the dehydration reaction, both the β-ASSM and TSSM lose the OC_6H_4 group, then, successively lose the OC_6H_4 group, the –CH=N and $-CH_2CH_2-$ group along the main chain of the Schiff base. Lastly, the pyrolytic product is MgO and the mixture of MgO and $MgSO_4$. Obviously, the thermal decomposition process of the α-ASSM is very different from that of the β-ASSM and TSSM. Both in the alanine-salicylal Schiff base and in the taurine-salicylal Schiff base, the OC_6H_4 group is at the terminal of the Schiff base molecule. Generally, the group at the terminal in the main chain of the molecule or one in the branched chain of the molecule is more easily eliminated from the molecule in the thermal decomposition process. This is just why the β-ASSM and TSSM lose the OC_6H_4 group easily and why the $-CH_3$ group in the branched main of the α-alanine-salicylal Schiff base is eliminated after the dehydration reaction. However, why does the α-ASSM lose the $-C_6H_4$ group, but does not lose the OC_6H_4 group in the thermal decomposition process? Perhaps, this indicates that the O atom of the OC_6H_4 group in the α-alanine-salicylal Schiff base bonds with the Mg ion. Because, the formation of the Mg–O bond between the Mg ion and O atom of the OC_6H_4 group can weaken the bonding of the O to the C_6H_4 group. This must make the $-C_6H_4$ group be eliminated more easily from the molecule chain. At same time, the O atom of the OC_6H_4 group can not be eliminated due to the bonding of this O atom to the Mg ion. This conclusion can be supported by the results of infrared spectra. As is mentioned above, in the infrared spectrum of the α-ASSM, there are two strong absorption peaks from the stretching vibrations of the Mg–O bonds. The peak at 539 cm^{-1} can be assigned to the stretching vibration of the Mg–O bond between the Mg and O atom of the $-COO^{-1}$ carboxyl group and that at 428 cm^{-1} can be assigned to the

Table 5 Thermal decomposition data of the Schiff base complexes of Mg

Reaction	*T*(DTA)/°C	Mass loss/%	
		$W_{exp.}$	$W_{theor.}$
$Mg[OC_6H_4CHNCH(CH_3)COO]\cdot 2H_2O$			
$\downarrow -H_2O$	152 (endo.)	8.7	7.2
$Mg[OC_6H_4CHNCH(CH_3)COO]\cdot H_2O$			
$\downarrow -H_2O$	207 (endo.)	7.3	7.2
$Mg[OC_6H_4CHNCH(CH_3)COO]$			
$\downarrow -CH_3, -CH$		11.3	11.2
$Mg[OC_6H_4CHNCOO]$			
$\downarrow -CHN$	388 (exo.)	11.0	10.7
$Mg[OC_6H_4COO]$			
$\downarrow -C_6H_4$	396 (exo.)	30.8	30.2
$MgCO_3$			
$\downarrow -0.75CO_2$		12.0	13.1
$0.75MgO+0.25MgCO_3$			
$\downarrow -0.25CO_2$		3.7	4.3
MgO		15.2	16.1
$Mg[OC_6H_4CHNCH_2CH_2COO]\cdot 2H_2O$			
$\downarrow -2H_2O$	138 (endo.)	14.4	14.3
$Mg[OC_6H_4CHNCH_2CH_2COO]$			
$\downarrow -OC_6H_4$	420 (exo.)	36.4	36.6
$Mg[CHNCH_2CH_2COO]$			
$\downarrow -CHN$		10.3	10.7
$Mg[CH_2CH_2COO]$			
$\downarrow -CH_2CH_2$	517 (exo.)	11.7	11.1
Mg(CO)O			
$\downarrow -CO$		14.5	11.1
MgO		12.7	16.0
$Mg[OC_6H_4CHNCH_2CH_2SO_3]\cdot 2H_2O$			
$\downarrow -2H_2O$	117 (endo.)	12.3	12.5
$Mg[OC_6H_4CHNCH_2CH_2SO_3]$			
$\downarrow -OC_6H_4$	419 (exo.)	31.6	32.0
$Mg[CHNCH_2CH_2SO_3]$			
$\downarrow -CHN$		9.6	9.4
$Mg[CH_2CH_2SO_3]$			
$\downarrow -CH_2CH_2$	509 (exo.)	10.3	10.3
$MgSO_3$			
$\downarrow -0.5SO$		8.6	8.3
$0.5MgO+0.5MgSO_4$		27.6	28.0

stretching vibration of the Mg–O bond between the Mg and O atom of the OC_6H_4 group. Why are the vibration frequencies of the two Mg–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, 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, if an O atom is bonded to a group with a very large molecular mass, when the O atom bonds with the M ion, the 'apparent mass' of the O atom seems to become larger than the mass of an O atom alone. The 'mass' of the $–C_6H_4$ group is much larger than that of $–COO^{-1}$ group. Therefore, we can reasonably assume that the frequency of the stretching vibration of the Mg–O bond between the Mg ion and the O atom of the OC_6H_4 group must be lower than that of the Mg–O bond between the Mg ion and the O atom of the $–COO^{-1}$ carboxyl group. Besides, the formation of the coordination bond between the Mg ion and the O atom of the OC_6H_4 group must also weaken the O=C bond between the O and C atom of the C_6H_4 group. Perhaps, this is just why the α-ASSM lose the C_6H_4 group, but not lose the OC_6H_4 group in the thermal decomposition process. However, why is not there the Mg–O bond between the Mg ion and the O atom of the OC_6H_4 group in the β-ASSM and TSSM? This may be because the molecular chain of the β-alanine-salicylal Schiff base and the taurine-salicylal Schiff base is longer. In this case, the O atom of the OC_6H_4 group at one terminal in the main chain of the Schiff base is far from the Mg ion at another terminal in the main chain. Hence, the Mg ion can only bond with the O atom of the carboxyl or sulfonate group of the Schiff base. If this conclusion is reasonable, we can explain why the thermal decomposition processes of the β-alanine-salicylal Schiff base complex and the taurine-salicylal Schiff base complex of magnesium are similar to each other, but very different from that of the α-alanine-salicylal Schiff base complex of Mg. So, we can consider that the thermal decomposition studies of the complexes can indicate that there are different coordination structures in the complexes.

Conclusions

New complexes of α-ASSM, β-ASSM and TSSM were synthesized. Crystalline phases and microstructure of these complexes were studied. X-ray diffraction patterns show that the crystal structures of the α-ASSM and β-ASSM belong to orthorhombic system, but that of the TSSM belongs to monoclinic system. Infrared spectra indicate the formation of the Schiff base. The thermal decomposition processes of the β-ASSM and TSSM are similar to each other, but very different from that of the α-ASSM. The results of thermal analysis and infrared spectra show that the Mg ion may bond not only with the O atom of the $–COO^{-1}$ carboxyl group, but also with the O atom of the OC_6H_4 group in the α-ASSM. However, the Mg ion bonds only with the O atom in the carboxyl or sulfonate group in the β-ASSM or TSSM.

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