Complexes of the selected transition metal ions with 4-methoxycinnamic acid

Physico-chemical properties

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Abstract In this study, 4-methoxycinnamates of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) were synthesised. From the infrared (IR) spectra analysis of complexes, sodium salt and according to the spectroscopic criteria the carboxylate groups seem to be bidentate chelating. The complexes of 4-methoxycinnamates lose the water molecules in one or two steps. The final products of their decomposition are oxides of the respective metals. The enthalpy values of dehydration process were determined. The FTIR spectra of the gas phase products indicate that the decomposition of the complexes is connected mainly with the release of molecules of water (H_2O), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4) and other hydrocarbons. The analysed compounds follow the Curie–Weiss law. The magnetic moment values experimentally determined change as follows: from 5.90 μ_B to 6.27 μ_B for Mn(II) complex, from 4.57 μ_B to 4.99 μ_B for Co(II) complex, from 3.68 μ_B to 3.30 μ_B for Ni(II) complex, from 1.87 μ_B to 1.96 μ_B for Cu(II) complex, from 3.06 μ_B to 3.51 μ_B for Nd(III) complex, and from 6.91 μ_B to 6.90 μ_B for Gd(III) complex.

Introduction

Cinnamic acid (3-phenyl-2-propanoic acid) being a derivative of phenylalanine comprises a relatively large family of organic isomers [1]. It has antibacterial, antifungal and antiparasitic properties, and its derivatives are an important pharmaceuticals for high blood pressure and stroke prevention having antitumour activity [2–5]. From the survey of literature, it follows that there are articles that mainly deal with the study of cinnamic acid structure, its properties, derivatives and complexes with alkali metals, such as Zn(II), Hg(I), Hg(II), Cd(II), and Zn(II) [2–10]. Having very important biological activity and specific structure, cinnamic acid has been still extensively and solidly studied.

4-Methoxycinnamic acid as derivative of cinnamic acid is used in cosmetology and medicine as antibacterial agent [11, 12]. Its esters were also applied in the perfumer's industry as essential components of aromatic substance, perfumes and pharmaceuticals [13]. Moreover, they are used for synthetic indigo production as well. 4-Methoxycinnamic acid may be also applied as optical filter or it may deactivate molecules exited by light to protect the polymers and other organic substance [14, 15]. In cosmetics, 4-methoxycinnamates are used for the protection of skin against UV-A and UV-B radiation [16, 17].

In our experiments, the complexes obtained as microcrystalline powder are characterised by elemental analysis, infrared (IR) spectral data, thermal studies and X-ray diffraction measurements. Thermal characterizations allowed

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us to evaluate the assumed position of crystallization water molecules in outer or inner spheres of complex coordination, determine the endo- or exoeffects connected with such processes as dehydration, melting, oxidation, reduction and estimate the strength of bonding between atoms or groups of atoms and ions. The magnetic susceptibility were measured to study the nature of coordination of the central ions and ligands to get information whether the analysed complexes are of low or high spin or if the ligands form the strong or weak fields and if the analysed compounds are monomers or dimers.

Experimental

Materials

The complexes of 4-methoxycinnamic acid anion with of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) were prepared by the addition of the equivalent quantities of 0.1 M ammonium 4-methoxycinnamate (pH ~ 5) to a hot solution containing the Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) chlorides and crystallizing at 20 °C. In order to obtain the Nd(III) and Gd(III) chlorides the Nd_2O_3 and Gd_2O_3 (99.9% pure, Aldrich Chemical Company) samples of 0.8 g was separately digested in the equivalent volumes (0.44 and 0.41 cm^3, respectively) of concentrated HCl (35–38% pure, $d = 1.18$ g/cm^3, Polish Chemical Reagents in Gliwice (Poland)). The solution was constantly heated. The rare earth(III) chloride was practically evaporated to dryness. The residue was dissolved in water forming the solution of lanthanide(III) chloride, pH value of which was equal to ~5. To the hot solutions of chlorides, the equivalent amounts of 0.1 M ammonium 4-methoxycinnamate were added.

4-Methoxycinnamate of ammonium (pH ~ 5) of 0.1 M concentration was prepared by the addition of concentrated solution of NH_3aq (25% pure, Polish Chemical Reagents in Gliwice (Poland)) to 4-methoxycinnamic acid water solution (99% pure, Aldrich Chemical Company).

In order to reach the equilibrium state the solids were heated for 1 h at 50–60 °C with constant stirring. Next they were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 30 °C to a constant mass.

The 4-methoxycinnamate of Na(I) was prepared by the addition of equivalent amount of 0.1 M ammonium 4-methoxycinnamate to NaOH solution containing 1 g NaOH (analytically pure, Polish Chemical Reagents in Gliwice (Poland)).

For the preparation of the complexes, the following chlorides of d-block elements were used: $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $CdCl_2 \cdot 6H_2O$ (analytically pure, REAGENTS—Chemical Enterprise in Lublin (Poland)).

Methods

The contents of carbon and hydrogen were determined by elemental analysis using a CHN 2400 Perkin–Elmer analyser. In order to estimate if analysed complexes were obtained in the pure form without Cl(I) ions, the Schöniger method for chloride content determination was used. The contents of M(II) and M(III) metals were established by means of ED XRF spectrophotometer (Canberra-Packard) (Table 1).

The IR spectra of complexes were recorded over the range of 4,000–400 cm^{-1} using M-80 spectrophotometer (Carl Zeiss, Jena). Samples for IR spectra measurements were prepared as KBr discs.

The thermal stability and decomposition of the complexes were studied in air using Setsys 16/18 (Setaram)TG, DTG and DSC instruments. The experiments were carried out two times under air flow in the temperature range of 20–700 °C at a heating rate of 10 °C min^{-1}. The initial mass of samples of 4-methoxycinnamates of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) used for measurements were following: Mn(II), 7.52 mg; Co(II), 7.65 mg; Ni(II), 7.21 mg; Cu(II), 7.29 mg; Cd(II), 7.42 mg; Nd(III), 8.64 mg; and Gd(III), 7.96 mg. Samples of the compounds were heated in Al_2O_3 crucibles. The ranges of temperature of complex decompositions were determined by computer program. The TG-FTIR measurements were also made in the nitrogen atmosphere with the use of Q5000 instrument (Firm TA Instruments) with Nicolet 6700 Spectrophotometer. The experiments were carried out in Pt crucibles under nitrogen flow of 25 mL min^{-1} at a measurement heating rate of 15 °C min^{-1}. The masses of samples in experiments were following: Mn(II), 6.321 mg; Co(II), 7.079 mg; Ni(II), 3.793 mg; Cu(II), 5.492 mg; Cd(II), 4.528 mg; Nd(III), 6.401 mg; and Gd(III), 5.257 mg. The thermal stability for the analysed complexes was also studied in the range of

Table 1 Elemental analysis data of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) 4-methoxycinnamates

Complex	C/%		H/%		M/%	
L = $C_{10}H_9O_3$	Calcd.	Found	Calcd.	Found	Calcd.	Found
$MnL_2 \cdot 2H_2O$	53.00	52.50	4.94	4.90	12.00	11.75
$CoL_2 \cdot 2H_2O$	53.46	53.01	4.90	4.67	13.12	13.20
$NiL_2 \cdot H_2O$	55.70	54.99	4.64	4.29	13.67	13.46
$CuL_2 \cdot H_2O$	55.04	55.00	4.58	4.60	14.67	14.50
$CdL_2 \cdot 2H_2O$	47.00	46.90	4.38	4.07	22.31	22.00
$NdL_3 \cdot H_2O$	51.93	51.73	4.18	3.84	20.80	20.73
$GdL_3 \cdot 2H_2O$	49.72	49.29	4.28	4.03	21.68	21.48

25–250 °C in the air atmosphere at a heating rate of 5 °C min^{-1}. The masses of complexes used for measurements were following: Mn(II), 8.24 mg; Co(II), 7.94 mg; Ni(II), 6.92 mg; Cu(II), 7.70 mg; Cd(II), 8.21 mg; Nd(III), 8.07 mg; and Gd(III), 7.27 mg. Magnetic susceptibilities of polycrystalline samples of 4-methoxycinnamates of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) were investigated at −196 to 30 °C. The measurements were carried out using the Gouy's method. Weight changes were obtained from Cahn RM-2 electrobalance. The calibrant employed was Hg[Co(SCN)$_4$] for which the magnetic susceptibility was assumed to be 1.644×10^{-5} cm^3 g^{-1}. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [18].

Results and discussion

4-Methoxycinnamates of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) were obtained as polycrystalline solids. The metal ion-to-ligand mole ratio is 1:2 and 1:3 in the case for d-electron metal complexes and those of 4f metal ion (Nd(III) and Gd(III)) compounds, respectively. Their formulae are ML$_2$·nH$_2$O and ML$_3$·nH$_2$O, where L = C$_{10}$O$_3$H$_9$, and n = 2 for M(II) = Mn, Co, Cd and M(III) = Gd, and n = 1 for M(II) = Ni, Cu and M(III) = Nd. Their colours are the following: pale pink for Mn(II), pink for Co(II), green for Ni(II), blue for Cu(II), yellow for Cd(II), violet for Nd(III) and white for Gd(III).

IR spectra

The IR spectra of 4-methoxycinnamic acid, 4-methoxycinnamates of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III), Gd(III) and for sodium salt were recorded. Their

Table 2 Wavenumbers (cm^{-1}) of COO$^-$ and M–O bands in the analysed complexes of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III), Gd(III) and Na and that of the COOH band in 4-methoxycinnamic acid

Compound L = C$_{10}$H$_9$O$_3$	C=O	v_{as}OCO	v_sOCO	ΔvOCO	v(M–O)
MnL$_2$·2H$_2$O	–	1536	1412	124	520
CoL$_2$·2H$_2$O	–	1536	1412	124	548
NiL$_2$·H$_2$O	–	1544	1408	136	520
CuL$_2$·H$_2$O	–	1550	1410	140	520
CdL$_2$·2H$_2$O	–	1532	1408	124	516
NdL$_3$·H$_2$O	–	1532	1400	132	556
GdL$_3$·2H$_2$O	–	1528	1392	136	560
NaL	–	1552	1408	144	–
HL	1688	–	–	–	–

interpretation was made according to the literature [19–31]. Some results of their IR spectra analysis are presented in Table 2 and Fig. 1. The IR spectrum of 4-methoxycinnamic acid shows the following absorption bands: a strong band of COOH at 1,688 cm^{-1}, the bands assigned to asymmetric and symmetric vibrations of CH$_3$ group at 2,972–2,936 and 2,844–2,820 cm^{-1}, respectively, the
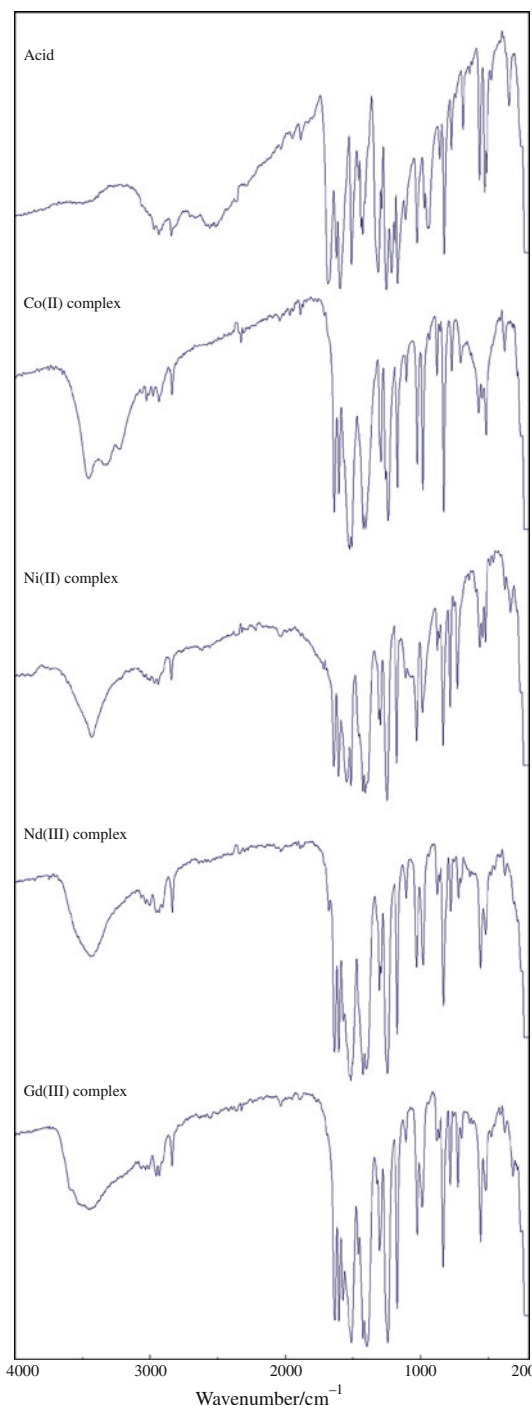

Fig. 1 IR spectra for 4-methoxycinnamic acid and 4-methoxycinnamates of Co(II), Ni(II), Nd(III) and Gd(III)

bands of v(C–C) vibrations at 1624, 1596, 1512, 1444 and 1028 cm^{-1}, the bands of v(C–H) vibrations at 1,288 cm^{-1}, β(C–H) vibration at 1,192 cm^{-1} and the bands of –C–O–C– at 1,172 cm^{-1} and –C=C– vibrations at 1,428 cm^{-1}, the bands of skeleton vibrations occur at 688 and 568 cm^{-1}. In the IR spectra of 4-methoxycinnamates, the band at 1,688 cm^{-1} disappears, which confirms that no COOH is present in the complexes. The intense broad absorption bands at 3,600–3,372 cm^{-1} indicate the presence of water molecules. The bands arising from asymmetric and symmetric vibrations of OCO$^-$ group occur at 1,550–1,528 and 1,412–1,392 cm^{-1}, respectively. The bands at 2,980–2,932 and 2,856–2,836 cm^{-1} are assigned to asymmetric and symmetric vibrations of CH$_3$ group. The bands at 1,422 cm^{-1} result from the –C=C– vibrations and those at 1,192–1,172 cm^{-1} are assigned to –C–O–C– vibrations.

The bands at 560–516 cm^{-1} confirm the metal–oxygen ionic bond. According to literature, these type of bands may be partially coupled with C–OCH$_3$ banding while those of pure M–O stretching vibration may occur also at lower frequencies [23, 27, 30]. It appears that the bands of M–O stretching vibrations of Mn(II), Co(II), Ni(II) and Cu(II) complexes may occur in the range of 685–535 cm^{-1} depending on the structure of complex coordination spheres and kind of ligands [27].

The magnitudes of separation, ΔvOCO, between the frequencies of v_{as}OCO and v_sOCO in the IR spectra of complexes are lower (ΔvOCO = 140–124 cm^{-1}) than that in the sodium salt (Δv = 144 cm^{-1}) which may indicate a smaller degree of ionic bond in the 4-methoxycinnamates of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) compared to that in the sodium salt. According to the literature, sodium and potassium salt of carboxylic acids are considered to be ionic with their structure and M–O type bonding [30]. Therefore, their IR spectra for unidentate carboxylate group show a large increase in the asymmetric stretching OCO$^-$ and a similar decrease in the symmetric stretching OCO$^-$ frequencies [27, 29, 30]. The smaller values of ΔvOCO for the complex than that for sodium salt indicate the decrease of ionic M–O type bonding and the increase of its covalent character [27, 29, 30].

Table 2 shows that in the case of 4-methoxycinnamates of Mn(II), Co(II) and Cu(II) the bands of v_{as}OCO and v_sOCO are shifted to lower and higher frequencies, respectively, compared to those for the sodium 4-methoxycinnamate (v_{as}OCO = 1,552 cm^{-1} and v_sOCO = 1,408 cm^{-1}), while for the complexes of Nd(III) and Gd(III) they have the lower values of frequencies than those in the sodium salt IR spectrum.

In the case of Ni(II) and Cd(II) compounds, the bands of v_{as}OCO are removed to lower frequencies, whereas those of v_sOCO have the same values compared to those in the sodium 4-methoxycinnamate. A general tendency in the

relationship between ΔvOCO (ΔvOCO = v_{as}OCO – v_sOCO) and the types of coordination of the OCO$^-$ group to metal ions by examining the structures and spectral data was observed for a number of acetate salts in the solid state [20, 22]. A general trend in this relationship may be summarised as follows:

(1) Structure of the carboxylate group is bidentate chelating when the bands of v_{as}OCO and v_sOCO in the analysed complex are shifted to lower and higher wavenumbers, compared to those for sodium salt; or ΔvOCO of studied complex $\ll \Delta v$OCO of sodium salt,

(2) Bidentate bridging structure exists when bands of v_{as}OCO and v_sOCO in studied complex are shifted to higher wavenumbers, compared to those for sodium salt; or ΔvOCO of studied complex $\approx \Delta v$OCO of sodium salt.

(3) For monodentate geometry of carboxylate group the bands of v_{as}OCO and v_sOCO in the analysed complex are shifted to higher and lower wavenumbers, respectively, compared to those for sodium salt; or ΔvOCO of studied complex $\gg \Delta v$OCO of sodium salt.

Therefore, according to Nakamoto and Manhas spectroscopic criteria presented above the carboxylate ion in the analysed complexes seems a bidentate chelating ligand probably also in the case of Cu(II) complex [27, 29, 30]. This conclusion as formulated mainly on the grounds of Nakamoto criterion despite the small difference of ΔvOCO for sodium salt (ΔvOCO = 144 cm^{-1}) and analysed Cu(II) compound (ΔvOCO = 140 cm^{-1}). Several bands of aromatic system as well as bands which derive from the –C=C– double bond are shifted towards the lower wavenumbers in the spectra of complexes compared to the spectrum of acid. These kinds of displacement may be generally interpreted as a decrease in the force constants of bonds which results from a decrease of electronic charge density around atoms [23].

Thermal analysis

The thermal properties of the 4-methoxycinnamates of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) were investigated by means of TG, DTG and DSC technique in air in the range of 20–700 °C and also at 25–250 °C. The ranges of temperature of complex decompositions were determined by computer program. The FTIR spectra of the gas phase products were recorded as well in nitrogen atmosphere.

Their thermal stability was also preliminary investigated by heating their samples in the ceramic crucibles. They were found to decompose with melting process being clearly observed during heating. Some results of the

Table 3 Temperature range of thermal stability of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) 4-methoxycinnamates in air

L = $C_{10}H_9O_3$	$\Delta T_1/°C$	Mass loss/%		n	$\Delta T_2/°C$	Mass loss/%		ΔH/kJ mol^{-1}	$T_k/°C$	Final product of decomposition
		Calcd.	Found			Calcd.	Found			
$MnL_2 \cdot 2H_2O$	116–135	8.00	8.16	2	326–463	83.00	82.99	86.75	467	Mn_2O_3
$CoL_2 \cdot 2H_2O$	105–145	8.01	7.92	2	320–456	80.90	81.77	97.09	462	CoO
$NiL_2 \cdot H_2O$	175–208	4.17	4.25	1	278–417	84.00	84.20	46.31	420	NiO
$CuL_2 \cdot H_2O$	170–207	4.12	3.05	1	281–522	75.00	74.50	20.27	522	CuO
$CdL_2 \cdot 2H_2O$	100–130	7.17	7.10	2	287–517	74.50	74.49	89.37	520	CdO
$NdL_3 \cdot H_2O$	100–130	2.59	2.99	1	329–540	75.90	75.84	31.94	620	Nd_2O_3
$GdL_3 \cdot 2H_2O$	75–106	3.72	4.18	1.5	329–529	71.00	70.91	16.71	617	Gd_2O_3
	106–125	1.24	1.30	0.5				5.57		

ΔT_1 temperature range of dehydration process, n number of water molecules, ΔT_2 temperature range of complex decomposition, ΔH enthalpy value of dehydration process, T_k final temperature of decomposition process
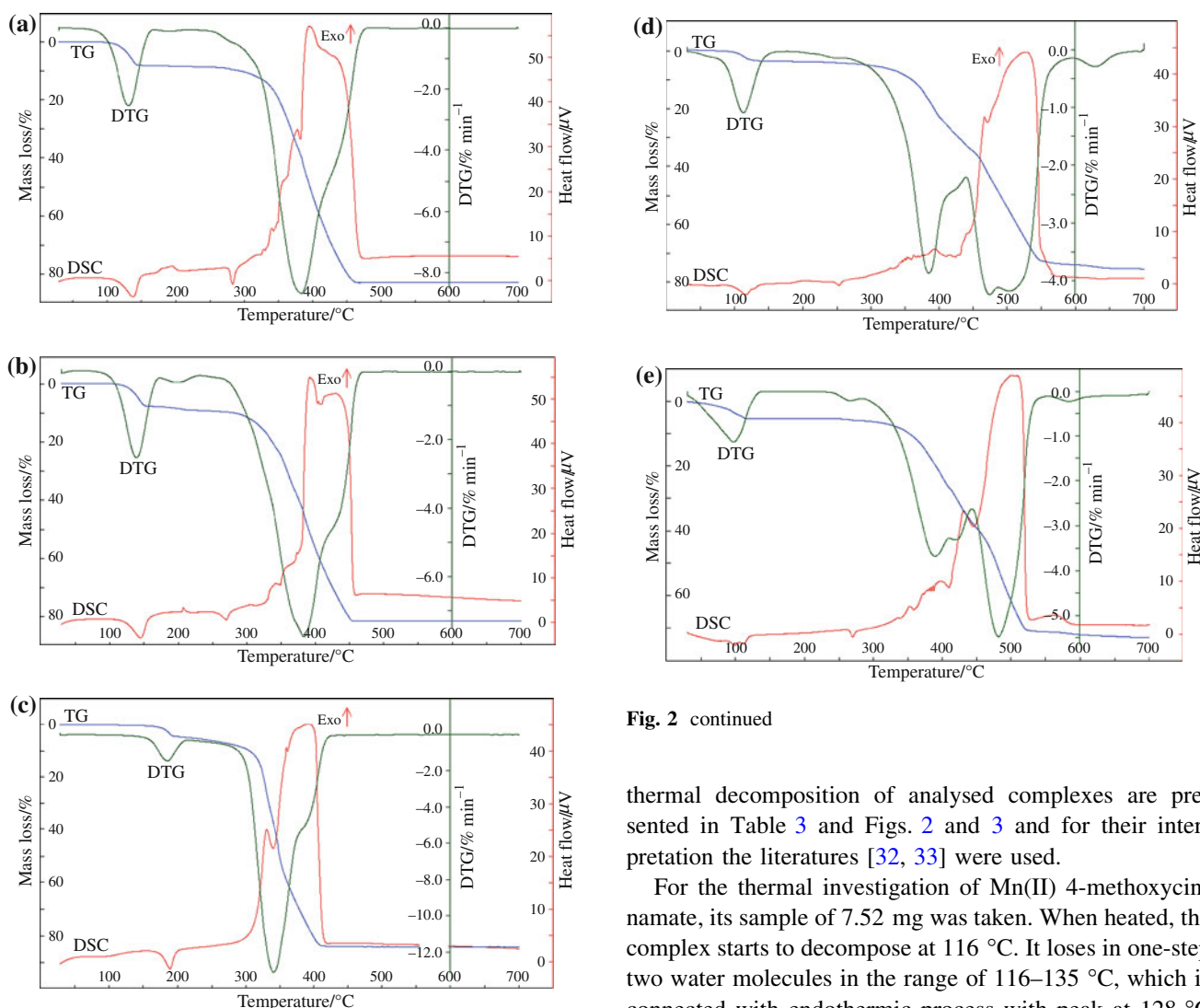

Fig. 2 TG, DTG and DSC curves: **a** $MnL_2 \cdot 2H_2O$; **b** $CoL_2 \cdot 2H_2O$; **c** $NiL_2 \cdot H_2O$; **d** $NdL_3 \cdot H_2O$; **e** $GdL_3 \cdot 2H_2O$ in air atmosphere

Fig. 2 continued

thermal decomposition of analysed complexes are presented in Table 3 and Figs. 2 and 3 and for their interpretation the literatures [32, 33] were used.

For the thermal investigation of Mn(II) 4-methoxycinnamate, its sample of 7.52 mg was taken. When heated, the complex starts to decompose at 116 °C. It loses in one-step two water molecules in the range of 116–135 °C, which is connected with endothermic process with peak at 128 °C on DSC curve. The loss of mass found from TG curve is equal to 8.16% (calcd. 8.00%) which corresponds to the

release of two water molecules (Fig. 2a). The average value of enthalpy for dehydration process of this complex, ΔH, is equal to 86.75 kJ mol^{-1} and that for one molecule of water 43.37 kJ mol^{-1}. In the temperature range of 278–292 °C, the melting process with endothermic peak at 283 °C (DSC curve) takes place. No loss of mass is observed on TG curve. The complex of Mn(II) in its second step of decomposition eliminates gradually organic ligands in the range of 326–463 °C with the exothermic effect on DSC curve and ultimately forms the Mn$_2$O$_3$ at 467 °C. The loss of mass determined from TG curve is equal to 82.99% while calculated 83.00% which confirms the Mn$_2$O$_3$ formation. The final product was identified by comparing its IR spectrum with that of the pure oxide.

The thermal investigation of Co(II) 4-methoxycinnamate was studied with the use of its sample of 7.65 mg. On heating the complex also releases two water molecules in one-step (105–145 °C). The dehydration process is accompanied by endothermic effect with peak at 136 °C (DSC curve). The loss of weight found from TG curve is 7.92% and calculated as 8.01%. These values confirm the release of two water molecules (Figs. 2b, 3a). The further heating of Co(II) compound leads to its melting with

endothermic peak at 267 °C. The TG curve gains the constant level and no mass loss is observed. In the second stage of decomposition 4-methoxycinnamate of Co(II) gradually releases the organic ligands at 320–456 °C with strong exothermic effect (DSC curve). The mass loss calculated from TG curve is equal to 81.77% (theoretical 80.90%) indicates the formation of CoO to be final product of decomposition. It was identified by spectroscopic method. The final temperature of Co(II) oxide formation is equal to 462 °C. The value of enthalpy determined for dehydration process of Co(II) is 97.09 kJ mol^{-1} and that for one molecule of water 48.54 kJ mol^{-1}.

The 4-methoxycinnamate of Ni(II) also decomposed in two stages (Fig. 2c). For the measurement, its sample of 7.21 mg was used. In the first step, the dehydration process occurs in the temperature range of 175–208 °C. The experimentally found loss of mass is equal to 4.25%, while the calculated one is 4.17% which corresponds to release of one water molecule. Next in the second step of Ni(II) complex decomposition, the organic ligands are eliminated in the range of 278–417 °C, and the final product NiO is formed (420 °C). The found mass loss is equal to 84.20%, while theoretical one is 84.00%. The average value of dehydration process is equal to 46.31 kJ mol^{-1}.

The 4-methoxycinnamate of Cu(II) is decomposed in two steps. Its sample of 7.29 mg was used for experiment. The first step of thermal decomposition of this complex starts at 170 °C with the elimination of one water molecule (found 3.05%; calcd. 4.12%) and with the endothermic effect with the peak at 187 °C. The average value of enthalpy for this process is 20.27 kJ mol^{-1}. In the second step, the Cu(II) complex releasing partially organic ligands with strong exothermic effect at 281–522 °C forms ultimately CuO (522 °C). The calculated loss of mass is equal to 75.00% and that of found is 74.50%, confirming CuO formation.

For the thermal analysis of Cd(II) 4-methoxycinnamate, the sample of 7.42 mg was used. From the obtained data, it was found that it is decomposed in two stages. At first, the dehydration takes place at 100–130 °C with endothermic peak at 123 °C. The found loss of mass is equal to 7.10% (calcd. 7.17%) which corresponds to the removal of two water molecules coordinated to metal ion. Next in the second step of decomposition during further heating, the complex loses the organic ligands with the exothermic effect in the range of 287–517 °C and forms CdO (at 520 °C) that is the final product of thermal decomposition (found 74.49%; calcd. 74.50%). During heating the Cd(II) complex melts above 258 °C without mass change on TG curve (endothermic peak at 269 °C). The value of enthalpy determined for this complex is equal to 89.37 kJ mol^{-1} and that for one molecule of water is 44.68 kJ mol^{-1}.

Figure 2d presents the TG and DSC curves of Nd(III) 4-methoxycinnamate. For the experiment, its sample of

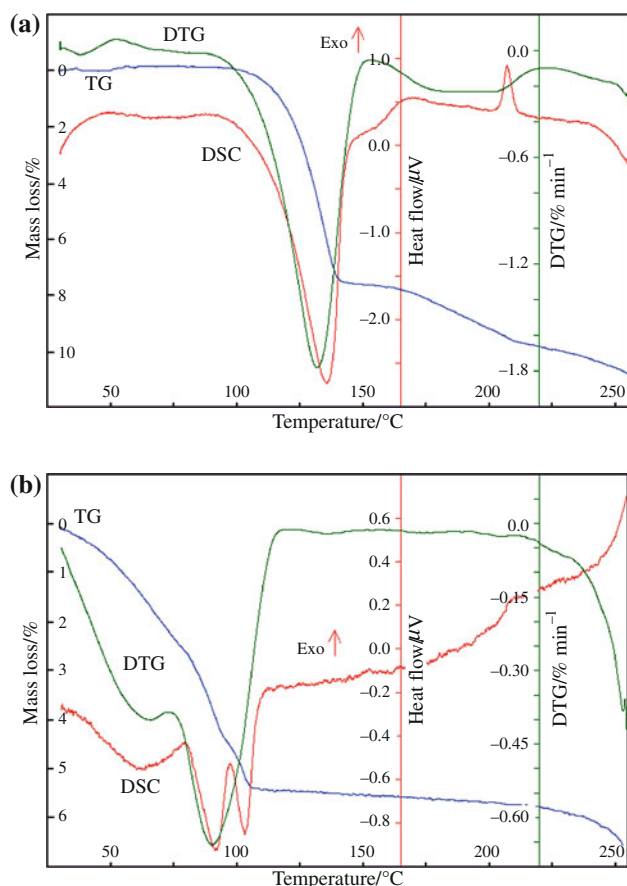**Fig. 3** TG, DTG and DSC curves of the **a** CoL$_2$·2H$_2$O; **b** GdL$_3$·2H$_2$O in air atmosphere

8.64 mg was taken. This complex is decomposed in two stages. In the range of 100–130 °C, the Nd(III) compound releases one water molecule in one step (found 2.99%; calcd. 2.59%). The endothermic peak connected with this process occurs at 112 °C (DSC curve). The value of enthalpy for that dehydration process is equal to 31.94 kJ mol^{-1}. The second stage of its decomposition occurs at 329–540 °C finally with the formation of Nd_2O_3 at 620 °C. The found loss of mass is 75.84% (calcd. 75.90%) which corresponds to neodymium(III) oxide formation.

For the thermal decomposition of Gd(III) 4-methoxycinnamate, the sample of 7.96 mg was taken. It decomposes in three steps (Figs. 2e, 3b). Firstly, the molecules of water are removed in two steps in the ranges of 75–106 and 106–125 °C with two endothermic peaks at 105 and 112 °C, respectively. In the first step, 1.5 molecule of water are being released (found 4.18%; calcd. 3.72%), while in the second one only 0.5 of its molecule (found 1.30%; calcd. 1.24%). The values of enthalpy for these two dehydration stages are equal to 16.71 and 5.57 kJ mol^{-1}, respectively. During further heating, it melts with the endothermic peak at 270 °C without mass change on TG curve. Next, the Gd(III) complex gradually eliminating organic ligands forms Gd_2O_3 at 617 °C (found 70.91%; calcd. 71.00%).

The final products of 4-methoxycinnamates of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) were identified by the comparison of their X-ray powder patterns and IR spectra with those of the pure oxides.

The gaseous products released during complex decompositions reveal them to be the molecules of H_2O, CO_2, CO, CH_4 and other hydrocarbons. Their FTIR spectra were recorded. For example, the Figs. 4 and 5 show them for Co(II) and Ni(II) 4-methoxycinnamate decompositions. In the FTIR spectra recorded for gaseous products for all the analysed complex decompositions, the bands at 4,000–3,500 and 1,700–1,500 cm^{-1} (75–208 °C) confirm the presence of H_2O molecules in the complexes. At higher temperature, the bands at 2,250–2,500 and 600–750 cm^{-1}, respectively, result from CO_2 vibrations, whereas the bands observed at 2,000–2,200 cm^{-1} are characteristic peaks of CO. The absorbance peak of methane (CH_4) appears around 3,000 cm^{-1} [34, 35].

From the survey of literature on the structure and thermal properties of carboxylates of d- and 4f-electron elements containing water molecules, it is possible to state that analysed compounds form aquacomplexes because the water molecules are coordinated to the central ions [36–38].

Magnetic properties

The magnetic susceptibility of the 4-methoxycinnamates of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) was measured in the temperature range of −196 to 30 °C. The complexes of analysed elements follow the Curie–Weiss law, since the values of the magnetic susceptibility decrease with increasing temperature. The paramagnetic dependences of magnetic susceptibility values of the complexes as a function of temperatures are presented in Table 4. The effective magnetic moment values were calculated from the equation:

$$\mu_{eff} = 2.83(\chi_M \cdot T)^{1/2}$$

where μ_{eff} is effective magnetic moment, χ_M is magnetic susceptibility per molecule and T is absolute temperature

The values of the Weiss constant, θ, for all complexes were found to have a negative sign which probably arises from antiferromagnetic spin interaction or from a crystal field splitting of the paramagnetic spin state. This important statement was precisely described in the following literature [39–44]. The magnetic moment data are very close to the spin only values for the respective ions calculated from the equation $\mu_{eff} = [4s(s + 1)]^{1/2}$ in the absence of the magnetic interactions for present spin-system. The magnetic moment values experimentally determined at −196–30 °C for Mn(II), Co(II), Ni(II), Cu(II), Nd(III) and Gd(III) are given in Table 4. Their
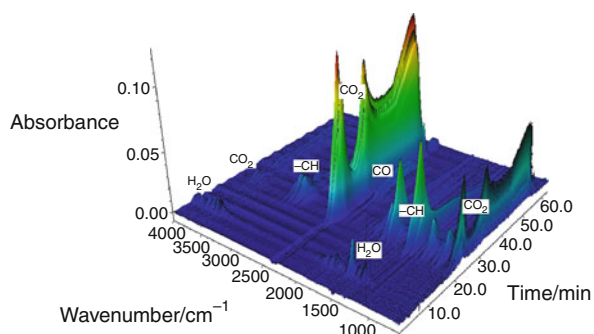

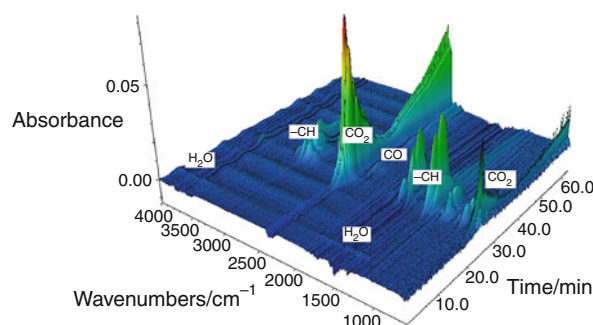Fig. 4 FTIR spectra of gaseous products for Co(II) 4-methoxycinnamate decomposition in N_2

Fig. 5 FTIR spectra of gaseous products for Nd(III) 4-methoxycinnamate decomposition in N_2

Table 4 Values of μ_{eff} and χ_M^{corr} for 4-methoxycinnamates of Mn(II), Co(II), Ni(II), Cu(II), Nd(III) and Gd(III)

MnL₂·2H₂O			CoL₂·2H₂O			NiL₂·H₂O			CuL₂·H₂O			NdL₃·H₂O			GdL₃·2H₂O		
$T/°C$	$\chi_M^{corr} \times 10^6$	μ_{eff}/μ_B	$T/°C$	$\chi_M^{corr} \times 10^6$	μ_{eff}/μ_B	$T/°C$	$\chi_M^{corr} \times 10^6$	μ_{eff}/μ_B	$T/°C$	$\chi_M^{corr} \times 10^6$	μ_{eff}/μ_B	$T/°C$	$\chi_M^{corr} \times 10^6$	μ_{eff}/μ_B	$T/°C$	$\chi_M^{corr} \times 10^6$	μ_{eff}/μ_B
−196	57261	5.90	−196	34246	4.57	−196	22268	3.68	−196	5747	1.87	−196	15432	3.06	−196	78431	6.91
−150	35156	5.88	−150	22046	4.66	−150	12146	3.46	−150	3483	1.85	−150	10235	3.18	−150	46597	6.78
−140	32747	5.91	−140	20307	4.65	−140	10838	3.40	−140	2967	1.88	−140	9393	3.16	−140	42147	6.70
−130	30633	5.92	−130	18580	4.61	−130	9985	3.38	−130	2750	1.87	−130	8898	3.19	−130	39428	6.72
−120	29027	5.96	−120	17420	4.62	−120	9322	3.38	−120	2875	1.88	−120	8428	3.21	−120	36352	6.67
−110	27463	5.99	−110	16569	4.65	−110	8829	3.39	−110	2709	1.88	−110	8057	3.24	−110	34072	6.67
−100	26090	6.01	−100	15779	4.68	−100	8336	3.40	−100	2581	1.88	−100	7685	3.26	−100	32149	6.67
−90	23976	5.93	−90	15101	4.70	−90	7881	3.40	−90	2433	1.89	−90	7388	3.29	−90	30721	6.71
−80	23152	5.98	−80	14497	4.73	−80	6934	3.27	−80	2341	1.90	−80	7091	3.31	−80	29238	6.72
−70	22159	6.00	−70	13941	4.76	−70	6611	3.28	−70	2212	1.90	−70	6844	3.34	−70	28221	6.77
−60	21377	6.04	−60	13448	4.79	−60	6270	3.27	−60	2139	1.91	−60	6522	3.34	−60	26875	6.77
−50	20574	6.06	−50	12905	4.80	−50	5967	3.26	−50	1991	1.89	−50	6349	3.37	−50	25529	6.75
−40	19771	6.07	−40	12424	4.82	−40	5720	3.27	−40	1936	1.90	−40	6151	3.39	−40	24568	6.77
−30	19073	6.09	−30	12005	4.83	−30	5493	3.27	−30	1863	1.90	−30	5928	3.40	−30	23634	6.78
−20	18524	6.13	−20	11684	4.87	−20	5303	3.28	−20	1826	1.92	−20	5755	3.41	−20	22755	6.79
−10	18017	6.16	−10	11363	4.89	−10	5095	3.28	−10	1789	1.94	−10	5607	3.44	−10	22123	6.83
0	17531	6.19	0	11055	4.92	0	4943	3.29	0	1734	1.99	0	5458	3.45	0	21492	6.85
10	17045	6.22	10	10796	4.95	10	4773	3.29	10	1697	1.94	10	5310	3.47	10	20640	6.84
20	16622	6.25	20	10549	4.98	20	4621	3.29	20	1660	1.96	20	5136	3.47	20	20393	6.92
30	16178	6.27	30	10278	4.99	30	4488	3.30	30	1586	1.96	30	5087	3.51	30	19597	6.90

$L = C_{10}H_9O_3$

values calculated at room temperature for Mn(II), Co(II), Ni(II), Cu(II), Nd(II) and Gd(III) ions are equal to 5.90 μ_B, 3.88 μ_B, 2.83 μ_B, 1.73 μ_B, 3.74 μ_B and 7.23 μ_B, respectively [39, 41]. For Mn(II), Co(II), Ni(II) and Cu(II) ions in analysed complexes the magnetic moment values are higher than the spin-only worth because they result from a spin-orbital coupling. The values of $\mu_{eff} = 5.90$–6.27 μ_B obtained for Mn(II) 4-methoxycinnamate suggest that it is high-spin compound with coordination number equals to 6. In the coordination sphere of Mn(II) ion there are probably two water molecules and two bidentate anions of 4-methoxycinnamic acid [6, 9]. This was confirmed by the IR spectral analysis from which it appears that the carboxylate groups are bidentate. The magnetic moments values of Co(II) 4-methoxycinnamate change from 4.57–4.99 μ_B. They confirm that it is also a high-spin complex with octahedral structure containing two molecules of water and two bidentate carboxylate groups in the coordination sphere of Co(II). Such character of carboxylate group was also confirmed by the IR spectral analysis as well (Table 2). In the case of Ni(II) 4-methoxycinnamate the magnetic moment values of complex change from 3.68 μ_B to $3.30\mu_B$ indicating that the Ni(II) ion exists in an octahedral triplet ground state with one molecule of water and two bidentate carboxylate groups coordinated to it. The IR spectrum reveals that the carboxylate groups in this compound are in fact bidentate. However, the coordination number of Ni(II) ion seems to be 5. The experimental data suggest that the compounds of Mn(II), Co(II) and Ni(II) are high-spin complexes with the weak ligand fields. In the octahedral coordination of Mn(II) ion there are four oxygen atoms of two carboxylate groups and two oxygen atoms of water molecules. The coordination numbers of Mn(II), Co(II), Ni(II), Cu(II), Nd(III) and Gd(III) ions could be established on the basis of the complete crystal structure determination of monocrystals but they have not been obtained. Not having full detailed data we may only consider the water molecule positions in analysed complexes [6, 9, 32, 33]. The magnetic susceptibility of Cu(II) complex changes with rising temperature according to the Curie–Weiss law and the observed effective moment at −196 °C is 1.87μ_B while that at room temperature is 1.96 μ_B. Copper in +2 oxidation state has only the spin magnetic moment of 1.73 μ_B but owing to spin orbit coupling, its higher values are often observed [39–44]. The results of μ_{eff} obtained for the Cu(II) complexes may also suggest its to be monomeric with the bidentate chelating carboxylate anion. The experimentally determined room temperature magnetic moment per Cu(II) in the analysed complex is similar to those observed for other monomeric Cu(II) compounds and is higher than the d^9 spin-only magnetic moment $\mu_{eff} = 1.73$ μ_B. This discrepancy is explained by the fact that spin-orbital coupling in the ion

can mix the ground state representing no orbital momentum, with higher levels of identical multiplicity. The participation of those higher levels results from a small orbital contribution in those cases where it is no to be expected. It may also indicate the operation of ferromagnetic interaction. The complex of Cd(II) is diamagnetic. In the case of Nd(III) and Gd(III) 4-methoxycinnamates the paramagnetic central ions remain practically unaffected by diamagnetic ligands coordinated around them. The f-electrons are outside influences and they do not participate in the formation of M–O bond. Their energy levels are the same as in the free ions. For Nd(III) and Gd(III) the ground state is separated by several hundred of cm^{-1} from the next higher lying state. Therefore the magnetic properties can be taken as those of the ground state alone. Taking into account this fact the Nd(III) and Gd(III) ions in analysed compounds act in the same way as the free ions. The values of μ_{eff} determined for Nd(III) and Gd(III) 4-methoxycinnamates are close to those calculated for them by Hund and Van Vleck [39]. Their values at room temperature for analysed complexes are: 3.47 μ_B for Nd(III) and 6.92 μ_B for Gd(III). From values of magnetic moments determined for these complexes it appears that the energies of 4f electrons in the central ions are not changed compared to those in the free lanthanide ions. Thus, the colours of the complexes stay the same as those in the free lanthanide ions. The electron density in the molecules makes the f–f electronic transitions of the central ions to be those of the lowest energy and the absorption occurs at relatively high wavelengths. The 4f orbitals of Nd(III) and Gd(III) ions effectively shielded by the 5s^{2}5p^6 octet. Therefore the metal ligand bonding in analysed lanthanide complexes is mainly electrostatic in nature [43, 44].

Conclusions

4-Methoxycinnamates of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) were found to be complexes containing one or two water molecules. They are stable up to 75–175 °C. Next they lose molecules of water in one or two steps. The losses of mass calculated from TG curves are equal to 1.30–8.16% (the theoretical values 1.24–8.01%). The complex of Ni(II) is the most thermally stable compound since its initial temperature of dehydration is equal to 175 °C, while Gd(III) compound has the least thermal stability (75 °C). After the loss of water molecules the complexes of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Nd(III) and Gd(III) in air are stable up to 278–329 °C and next they decompose to the respective oxides: Mn_2O_3, CoO, NiO, CuO, CdO, Nd_2O_3 and Gd_2O_3. The gaseous products of complex decompositions were mainly identified as: H_2O, CO_2, CO, CH_4 and hydrocarbons. The magnetic properties

of the analysed compounds were studied, and they proved the compunds to be paramagnetic substances that obey Curie–Weiss law.

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References

1. Madhurambal G, Ravindran B, Mariappan M, Mojumdar SC. Thermal, UV and FTIR spectral studies in alkali metal. J Therm Anal Calorim. 2010;100:811–5.
2. Abdelmoty I, Buchholz V, Di L, Guo C, Kowitz K, Enkelmann V, Wegner G, Foxman BM. Polymorphism of cinnamic and α-truxillic acids. Cryst Growth Des. 2005;5:2210–7.
3. Fernandes MA, Levendis DC, Koning CB. Solvate and polymorphs of *ortho*-ethoxy-*trans*-cinnamic acid: the crystal and molecular structures. Cryst Eng. 2001;4:215–31.
4. Ahn S, Harris KDM, Kariuki BM, Zin DMS. Polymorphic phase transformation in the 3-bromo-*trans*-cinnamic acid system. J Solid State Chem. 2001;10:156–61.
5. Kalinowska M, Świsłocka R, Lewandowski W. The spectroscopic (FT-IR, FT-Raman and H, C NMR) and theoretical studies of cinnamic acid and alkali metal cinnamates. J Mol Struct. 2007;8:572–80.
6. Hosomi H, Ohba S, Ito Y. *cis*-Diaquabis(*trans*-cinnamato-O,O′)-zinc(II). Acta Crystallogr C Cryst Struct Commun. 2000;56:e123.
7. Ray PC. Second-order polarizability of *p*-substituted cinnamic acids. Chem Phys Lett. 1996;248:27–30.
8. Fernandes MA, Levendis DC, Schoening FRL. A new polymorph of *ortho*-ethoxy-*trans*-cinnamic acid: single-to-single-crystal phase transformation and mechanism. Acta Cryst B Struct Sci. 2004;B60:300–14.
9. Kalinowska M, Świsłocka R, Lewandowski W. Zn(II), Cd(II) and Hg(I) complexes of cinnamic acid: FT-IR, FT-Raman, ^{1}H and ^{13}C NMR studies. J Mol Struct. 2011. doi:10.1016/j.molstruc.2011.01.063.
10. Ravindran B, Madhurambal G, Mariappan M, Ramamurthi K, Mojumdar SC. Growth and characterization of mercury cinnamate single crystal. J Therm Anal Calorim. 2011. doi:10.1007/s.10973-011-1292-4.
11. Scheuer E, Warshaw E. Sunscreen allergy: a review of epidemiology, clinical characteristics, and responsible allergens. Dermatitis. 2006;17:3–11.
12. Wolski T, Pszczoła D, Baj T. Budleja Davida (Buddleja davidii Franch)—ozdobna roślina lecznicza o wielokierunkowym działaniu leczniczym. Postępy Fitoterapii. 2010;2:75–82.
13. Singh TS, Mitra S. Interaction of cinnamic acid derivatives with serum albumins: a fluorescence spectroscopic study. Spectrochim Acta A. 2011;78:942–8.
14. Svoboda A, Walterova D, Vostalova J. Ultraviolet light induced alternation to the skin. Biomed Pap Med Fac Univ Palaczy Olomouc Czechoslov Repub. 2006;150:25–38.
15. Salvador A, Chisvert A. Analytical survey on UV filters determination. Anal Chim Acta. 2005;537:1–14.
16. Levy SB. Sunscreens and photoprotection. http://www.emedicine.com (available on-line June 2011).
17. Klimowicz A, Bielecka-Grzela S, Czuba E, Żejmo M. Sunscreens—chemical structure and application. Ann Acad Med Stetin. 2007;53:11–5.
18. Figgis BN, Nyholm RS. A convenient solid for calibration of the Gouy magnetic susceptibility apparatus. J Chem Soc. 1958;4190–1.
19. Silverstein RM, Bassler GC, Morrill TC. Spectrometric identification of organic compounds. New York: Wiley; 1991.
20. Lewandowski W, Barańska H. Comparison of the influence of silver, iron(III) and chromium(III) on the aromatic system of benzoic and salicylic acids in hydrated and anhydrous complexes. Vib Spectrosc. 1991;2:211–20.
21. Köse DA, Necefoğlu H. Synthesis and characterization of bis(nicotinamide) m-hydroxybenzoate complexes of Co(II), Ni(II), Cu(II) and Zn(II). J Therm Anal Calorim. 2008;93:509–14.
22. Lewandowski W. Effect of lanthanides on the aromatic system of benzoic acid. Warsaw: Publications of Warsaw Agricultural University, SGGW-AR; 1986. p. 9–45.
23. Burger K. Coordination chemistry: experimental methods. Budapest: Akadèmiai Kiadó; 1973.
24. Bellamy LJ. The infrared spectra of complex molecules. London: Chapman and Hall Ltd; 1975.
25. Varsányi G. Assignments for vibrational spectra of 700 benzene derivatives. Budapest: Akademiai Kiadó; 1973.
26. Gaber M, Rehab AF, Badr-Eldeen DF. Spectral and thermal studies of new Co(II) and Ni(II) hexaaza and octaaza macrocyclic complexes. J Therm Anal Calorim. 2008;91:957–62.
27. Nakamoto K. Infrared and Raman spectra of inorganic and coordination compounds. Toronto: Wiley; 1997. p. 1–256.
28. Bridson AK. Inorganic spectroscopic methods. New York: Oxford University Press; 1998. p. 1–30.
29. Manhas BS, Trikha AK. Relationship between the direction of shifts in the carbon-oxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination. J Indian Chem Soc. 1982;59:315.
30. Mehrotra RC, Bohra R. Metal carboxylates. London: Academic Press; 1983. pp. 8–15, 48–121, 256–322.
31. Cross A, Jones AR. An introduction to practical infrared spectroscopy. London: Butterworths; 1969. p. 1–95.
32. Nikolaev AV, Logvinienko VA, Myachina LI. Thermal analysis. New York: Academic Press; 1969.
33. Paulik F. Special trends in thermal analysis. Chichester: Wiley; 1995. p. 3–98.
34. Xu T, Huang X. Study on combustion mechanism of asphalt binder by using TG-FTIR technique. Fuel. 2010;89:2185–90.
35. Tao L, Zhao G-B, Qian J, Qin Y-K. TG-FTIR characterization of pyrolysis of waste mixtures of paint and tar slag. J Hazard Mater. 2010;175:754–61.
36. Rzączyńska Z, Bartyzel A, Olszewska E, Sawka-Dobrowolska W. Synthesis and characterization of Co(II), Cu(II) and Zn(II) complexes with 1,2-cyclobutanedicarboxylic acid. Polyhedron. 2006;25:687–94.
37. Rzączyńska Z, Bartyzel A, Głowiak T. Synthesis and characterization of triaquabis(1,1-cyclobutadienedicarboxylato-O, O′, O″, O‴)dimanganese(II). Polyhedron. 2003;22:2595–9.
38. Stępniak K, Ferenc W, Cristóvão B, Lis T. Crystal structures of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II) and Zn(II). Ecl Quim. 2007;32:23–8.
39. Van Vleck JH. The theory of electronic and magnetic susceptibilities. Oxford: Oxford University Press; 1932. p. 239–41.
40. Kettle SFA. Physical inorganic chemistry: a coordination chemistry approach. Oxford: Oxford University Press; 2000.
41. Earnshaw A. Introduction to magnetochemistry. New York: Academic Press; 1968. p. 1–83.
42. Figgis BN, Lewis J. Progress in inorganic chemistry. New York: Interscience; 1964.
43. Sinha SP. Systematic and properties of the lanthanides. Dordrecht: Reidel Publishing Company; 1983. p. 7–125.
44. O'Connor I. Progress in inorganic chemistry. New York: Wiley; 1982. p. 203–76.