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SPECTRAL, MAGNETIC AND THERMAL INVESTIGATIONS OF SOME *d*-ELECTRON ELEMENT 3-METHOXY-4-METHYLBENZOATES

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Conditions for the preparation of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 3-methoxy-4-methylbenzoates were investigated and their quantitative composition and magnetic moments were determined. The IR spectra and powder diffraction patterns of the complexes prepared of general formula $M(C_9H_9O_3)_2\cdot nH_2O$ (n=2 for Mn, Co n=1 for Ni, Cu, n=0 for Zn, Cd) were prepared and their thermal decomposition in air was studied. Their solubility in water at 293 K is of the order 10^{-2} (Mn)–10^{-4} (Cu) mol dm^{-3}. IR spectra of the prepared 3-methoxy-4-methylbenzoates suggest that carboxylate groups are bidentate bridging. The magnetic moments for the paramagnetic complexes of Mn(II), Co(II), Ni(II) and Cu(II) attain values 5.50, 4.45, 3.16 and 1.79 B. M., respectively. During heating the hydrated complexes lose crystallization water molecules in one step and then the anhydrous complexes decompose directly to oxides MO and Mn_3O_4. Only Co(II) complex decomposes to Co_3O_4 with intermediate formation CoO.

Keywords: *complexes, d-electron elements, IR spectra, magnetic moments, 3-methoxy-4-methylbenzoic acid, thermal decomposition*

Introduction

3-Methoxy-4-methylbenzoic acid $C_6H_3(OCH_3)(CH_3)COOH$, is a crystalline solid, sparingly soluble in water [1]. Its compounds with metal ions are not well-known. The complexes of rare earth elements [2] have been prepared as crystalline solid with molar ratio of metal to organic ligand of 1:3 and general formula $Ln(C_9H_9O_3)_3\cdot nH_2O$ (where n=2 for Y, La–Er and n=0 for Tm–Lu) sparingly soluble in water. During heating dihydrated complexes lose crystallization water molecules in one (Y, La, Pr–Er) or two steps (Ce) and then all the anhydrous complexes decompose directly to oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7. IR spectra of the rare earth 3-methoxy-4-methylbenzoates suggest that carboxylate groups are bidentate chelating.

In the last years there were published some papers on thermal decomposition of metal carboxylates [3–8]. This work is a continuation of our study on the physico-chemical properties and thermal decomposition [9–15] of metal complexes with benzenecarboxylic acids. Its aim was to prepare solid Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 3-methoxy-4-methylbenzoates and examine some of their physico-chemical properties and thermal decomposition during heating in static air.

Experimental

3-Methoxy-4-methylbenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared by reaction of stoichiometric quantities of 0.2 M solution of ammonium 3-methoxy-4-methylbenzoate (pH 5.5) and 0.2 M solution of metal(II) chloride. The precipitate was formed during heating in mother solution. Then it was heating yet 0.5 h at 343–353 K, was filtered off, washed with hot water to remove NH_4^+ ions and dried at 303 K to a constant mass. The sodium salt was obtained by adding 3-methoxy-4-methylbenzoic acid to solution of NaOH and crystallizing at room temperature.

The carbon and hydrogen in the prepared complexes were determined by elemental analysis on a Perkin-Elmer CHN 2400 analyser. The metal(II) ion content was determined by AAS method using atomic absorption spectrophotometer AAS-3 (Carl Zeiss, Jena). The content of crystallization water molecules was determined from TG curves and by heating the samples isothermally at defined temperature to a constant mass. IR spectra of the complexes prepared and spectra of 3-methoxy-4-methylbenzoic acid and its sodium salt were recorded as KBr discs on FTIR 1725 PerkinElmer spectrophotometer (range 4000–400 cm^{-1}). The solubilities of the prepared complexes in water were determined at 293 K, preparing saturated solutions in isothermal conditions. The concentration of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions in saturated solutions were determined by AAS method. X-ray diffractograms of the prepared complexes and the products of their decomposition were recorded using diffractometer HZG-412. The magnetic susceptibility of the prepared complexes were measured on a magnetic balance (Scherwood Scientific MSB MK I) using as a standard

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Co[Hg(SCN)$_4$]. The thermal stability of the prepared complexes was investigated by method TG, DTG and DTA. Measurements were made with Q-1500 derivatograph by method described earlier [2]. The samples were heating in air to 1273 K.

Results and discussion

3-Methoxy-4-methylbenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared as solids with molar ratio of metal to organic ligand of 1.0:2.0 and general formula $M(C_6H_3(OCH_3)(CH_3)COO)_2\cdot nH_2O$, where n=2 for Mn(II) and Co(II), n=1 for Ni(II) and Cu(II) and n=0 for Zn(II) and Cd(II) (Table 1) having colour characteristic for hydrated metal ions. The prepared complexes are crystalline and have different structures. They are characterized by different solubility in water. Their solubilities change from 10^{-2} mol dm^{-3} for Mn(II) complex, 10^{-3} mol dm^{-3} for Co(II), Ni(II), Zn(II) and Cd(II) to 10^{-4} mol dm^{-3} for Cu(II) one (Table 1). Generally complexes of Cu(II) with different carboxylic acids are more sparingly soluble in water than the complexes of other 3d metal ions [14, 15].

The prepared 3-methoxy-4-methylbenzoates exhibit similar to each other IR spectra (Table 2) in two groups: Mn(II)–Cu(II) and Zn(II)–Cd(II) and have many bands. When the acid is converted to the complexes the absorption band C=O group at 1684 cm^{-1} disappears and the bands of asymmetrical (ν_{as}) and symmetrical (ν_s) vibration of OCO$^-$ group appear at 1560–1540 and 1425–1410 cm^{-1}, respectively, the bands of OCH$_3$ with max. at 1388–1384, 1288–1280, 1250–1248 cm^{-1} the bands of CH$_3$ group at 2920 and 2833–2830, 1408–1404, 1320–1316 cm^{-1} and bands of M–O bond at 580–550 cm^{-1}. In the IR spectra of the prepared complexes there are bands of aromatic ring 1610–1607, 1463–1460, 1172–1168, 1112–1106 and 1040 cm^{-1}, and the CH bands at 878–875, 818–812, 778–775 and 650–640 cm^{-1} [9–12]. These bands are shifted insignificantly (10–4 cm^{-1}) or do not change their position compared to the respective bond of 3-methoxy-4-methylbenzoic acid, what indicates that metal(II) ions have only a weak influence on the benzene ring. In the IR spectra of the prepared complexes of Mn(II), Co(II), Ni(II) and Cu(II) there are broad absorption bands of ν(OH) with max. at 3400 cm^{-1} and narrow bands δ(H$_2$O) at 1630–1620 cm^{-1}, that are characteristic for the hydrates. In the IR spectra of Zn(II) and Cd(II) these bands are absent, what confirms anhydrous character of these complexes.

The separation values ν_{as}(OCO) and ν_s(OCO) in the spectra of the prepared 3-methyl-4-methoxybenzoates (125–130 cm^{-1}) are similar to that for the sodium salt (130 cm^{-1}), what shows on the similar degree of ionic bond in the prepared complexes compared to

Table 1 Analytical data and solubilities in water at 293 K of 3-methoxy-4-methylbenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

Complex	*M*/%		C/%		H/%		Solubility/10^{-3} mol dm^{-3}
	calcd.	found	calcd.	found	calcd.	found	
$MnL_2\cdot 2H_2O$	13.05	13.00	51.31	51.30	5.27	5.30	14.50
$CoL_2\cdot 2H_2O$	13.86	14.00	50.83	51.00	5.17	5.00	10.50
$NiL_2\cdot H_2O$	14.43	14.40	53.11	53.00	4.92	4.90	10.50
$CuL_2\cdot H_2O$	15.44	15.40	52.48	52.55	4.86	4.90	0.65
ZnL_2	16.53	16.50	54.63	54.69	4.55	4.51	7.54
CdL_2	25.40	25.50	48.82	49.00	4.06	4.00	7.12

L*=[$C_6H_3(CH_3)(CH_3)COO^-$

Table 2 Frequencies of characteristic absorption bands in IR spectra and magnetic moment (B. M.) of 4-methoxy-2-methylbenzoates of Mn(II), Co(II), Cu(II), Zn(II), Cd(II) and Na(I) (cm^{-1})

Complex	ν(OH)	ν_{as}(OCO)	ν_s(OCO)	ν_{as}–ν_s	ν(M–O)	μ_{eff}/B. M.	*n*
$MnL_2{}^*\cdot 2H_2O$	3400	1550	1425	125	575	5.50	5
$CoL_2\cdot 2H_2O$	3400	1550	1425	125	575	4.45	3
$NiL_2\cdot H_2O$	3400	1550	1420	130	560	3.16	2
$CuL_2\cdot H_2O$	3400	1560	1410	150	580	1.79	1
ZnL_2	–	1550	1420	130	550	–	–
CdL_2	–	1540	1410	130	560	–	–
$NaL\cdot xH_2O$	3400	1516	1392	124	–	–	–

L*=[$C_6H_3(CH_3)(OCH_3)COO]^-$; n – number of unpaired electrons

Table 3 Data for dehydration and decomposition of 3-methoxy-4-methylbenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

Complex	ΔT_1/K	Mass loss/%		Loss of H_2O mol	ΔT_2/K	Mass loss/%		T_k/K
		calcd.	found			calcd.	found	
MnL_2*$\cdot 2H_2O$	318–390	9.00	9.5	2	497–999	80.17	80.2	999
$CoL_2\cdot 2H_2O$	320–398	8.47	8.5	2	420–958	79.37	79.2	958
$NiL_2\cdot H_2O$	328–423	4.42	4.4	1	428–823	80.78	80.2	823
$CuL_2\cdot H_2O$	353–397	4.37	4.4	1	489–895	79.78	80.1	895
ZnL_2					473–968	79.42	79.5	968
CdL_2					452–893	70.97	71.0	893

*L=$[C_6H_3(CH_3)(OCH_3)COO]^-$; ΔT_1 – temperature range of dehydration; ΔT_2 – temperature range of decomposition; T_k – temperature over which the oxides exist

the sodium salt [16–18]. Only for Cu(II) complex value of ν_{as}–ν_s (150 cm^{-1}) is a little bigger than for the sodium salt. The bands of asymmetric and symmetric vibrations of OCO groups are shifted to higher frequencies ($\Delta\nu_{as}$=24–38 cm^{-1}, $\Delta\nu_s$=18–33 cm^{-1}). From the shifts of ν_{as}(OCO) and ν_s(OCO) and values of (ν_{as}–ν_s) in the IR spectra of the prepared complexes compared to the bands for the sodium salt, it is possible to suggest that OCO groups are bonded as bidentate bridging [16–20] and the complexes exist as dimers or polymers. In the hydrated complexes there are probably inner sphere water molecules.

The susceptibilities of paramagnetic Mn(II), Co(II), Ni(II) and Cu(II) complexes calculated from results of magnetic measurements at 293 K were corrected by measuring the diamagnetic susceptibility of ligand. The magnetic moments were calculated by using formula $\mu_{eff}=2.84(X_M T)^{1/2}$. The complexes of Zn(II) and Cd(II) are diamagnetic. The magnetic moments determined for the complexes of Mn(II), Co(II), Ni(II) and Cu(II) are equal to 5.50, 4.45, 3.16 and 1.79 B. M., respectively (Table 2).The magnetic moment determined for Mn(II) 3-methoxy-4-methylbenzoate (5.5 B. M.) has lower value than theoretical one (5.91 B. M.) calculated for configuration d^5. The experimental values measured at room temperature for high spin octahedral structure of Mn(II) complexes are of the range 5.6–6.1 B. M. [17]. The small value of magnetic moment confirms dimeric or polymeric structure of this complex and permit to suggest that reduction of its value is caused by antiferric action Mn–Mn. For Co(II) and Ni(II) complexes the measured magnetic moments (4.45 and 3.16 B. M., respectively), differ to some extent from spin-only moments for d^7 and d^8 configurations (3 and 2 unpaired electrons) equal 3.87 and 2.83 B. M. Literature data [20, 21] show that measured magnetic moments for high spin Co(II) complex with octahedral structure attains values 4.3–5.28 B. M. and for octahedral structure of Ni(II) 2.8–3.5 B. M. This very high value of magnetic moment for Co(II) complex can be caused by coupling spin–orbital, which exist for elements of the first row of transition elements with configuration d^4–d^9. The magnetic moment determined for Cu(II) complex (1.79 B. M.) is similar to the theoretical (1.73 B. M.) and experimental values (1.7–2.2 B. M.) with configuration d^9 (one unpaired electron) [17, 18] and dimeric structure. The magnetic measurements confirms that in the hydrated 3-methoxy-4-methylbenzoates the water molecules are in inner sphere. Taking into account the octahedral structure of hydrated complexes it is possible to suggest that in dihydrated complexes water molecules act as monodentate ligand.

3-Methoxy-4-methylbenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are stable at room temperature. During heating they decompose in different ways (Table 3, Figs 1–3). Hydrated complexes are stable up to 318–328 K (Mn, Co, Ni) and 353 K (Cu). Dihydrated and monohydrated complexes lose crystallization water molecules in one step over the range 318–423 K forming anhydrous compounds. The dehy-

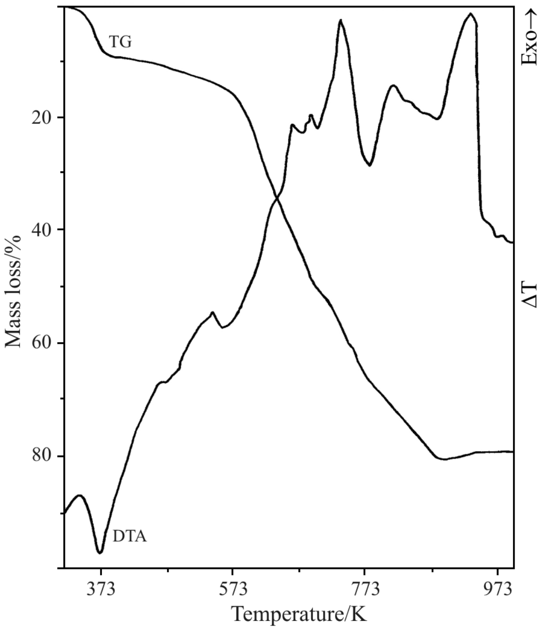

Fig. 1 TG, DTG and DTA curves of $Co(C_9H_9O_3)_2\cdot 2H_2O$

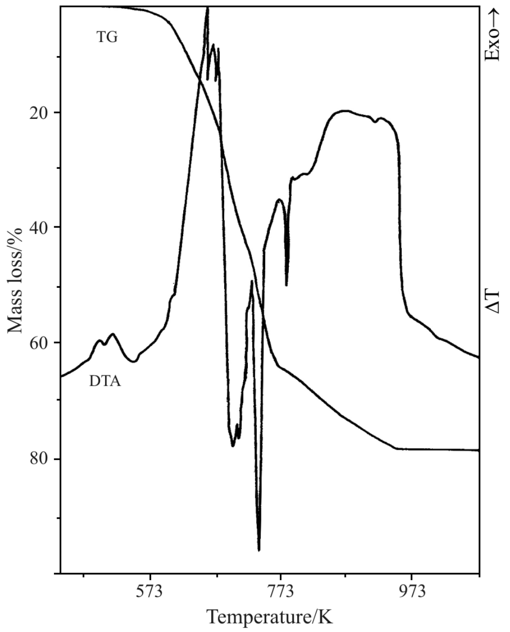

Fig. 2 TG, DTG and DTA curves of Zn($C_9H_9O_3$)

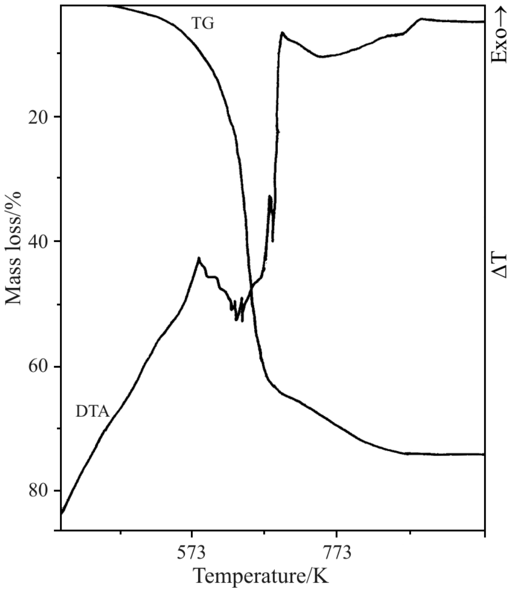

Fig. 3 TG, DTG and DTA curves of Cd($C_9H_9O_3$)

drated process is connected with strong endothermic effect. The anhydrous complexes are stable up to 427–498 K and next during heating decompose in one or two steps. Co(II) complex decomposes to Co_3O_4 with intermediate formation CoO. The complex of Mn(II) decomposes directly to Mn_3O_4, whereas these of Ni(II), Cu(II), Zn(II) and Cd(II) to oxides MO. The combustion of organic ligand and products of decomposition proceed with exothermic effects. The temperature over which oxides exist changes in the order: Ni<Cd<Cu<Co<Zn<Mn from 823 K for Ni(II) to 999 K for Mn(II).

The results obtained indicate that the prepared 3-methoxy-4-methylbenzoates decompose in the following way:

$$MnL_2{\cdot}2H_2O \rightarrow MnL_2 \rightarrow Mn_3O_4$$

$$CoL_2{\cdot}2H_2O \rightarrow CoL_2 \rightarrow CoO \rightarrow Co_3O_4$$

$$ML_2{\cdot}H_2O \rightarrow ML \rightarrow MO,\ M=\mathrm{Ni,\ Cu}$$

$$ML_2 \rightarrow MO,\ M=\mathrm{Zn,\ Cd}.$$

Conclusions

3-Methoxy-4-methylbenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared as solids with molar ratio of metal to organic ligand of 1.0:2.0. The complexes of Mn(II) and Co(II) were prepared as dihydrates, these of Ni(II) and Cu(II) as monohydrates, whereas the complexes of Zn(II) and Cd(II) as anhydrous ones. These complexes are characterized by different solubility in water. Their solubility in water at 293 K changes from 10^{-2} mol dm^{-3} for Mn(II) complex to 10^{-4} mol dm^{-3} for Cu(II) one. During heating hydrated complexes lose crystallization water molecules in one step and then the anhydrous complexes decompose directly to oxides MO and Mn_3O_4, whereas Co(II) complex decomposes to Co_3O_4 with intermediate formation CoO. The temperature of dehydration changes from 318 K for Mn(II) to 353 K for Cu(II) one. The temperature over which exist oxides changes from 823 K for Ni(II) complex to 999 K for Mn(II) one. The carboxylate groups in the studied complexes act probably as bidentate bridging and water molecules are in inner sphere of the complexes, and the complexes exist as dimers or polymers. The magnetic moments for paramagnetic complexes of Mn(II), Co(II), Ni(II) and Cu(II) attain values 5.50, 4.45, 3.16 and 1.79 B. M., respectively.

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