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Thermal, Spectral and Magnetic Investigations of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes with 4-Methoxy-2-methylbenzoic Acid

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Conditions for the preparation of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with 4-methoxy-2-methylbenzoic acid were investigated and their quantitative composition, magnetic moments and solubilities in water at 293 K were recorded. IR spectra and powder diffractograms of the complexes, prepared with molar ratio of metal to organic ligand of 1.0 : 2.0 and general formula $M(C_9H_9O_3)_2 \cdot nH_2O$, where n = 1 for Mn, Co, Ni, Cu, n = 2 for Cd and n = 0 for Zn, were recorded and their thermal decomposition in air was studied. During heating the complexes are dehydrated in one step and next the anhydrous complexes of Cu, Zn and Cd decompose directly to oxides (MO), whereas the complexes of Mn, Co and Ni decompose to oxides (Mn_3O_4, Co_3O_4, NiO) with intermediate formation of the mixture of free metals and their oxides. The effective magnetic moments the paramagnetic complexes of Mn(II), Co(II), Ni(II) and Cu(II) attain at 303 K values 5.65, 4.69, 3.18 and 1.27 B.M., respectively. On the basis of IR spectra it can be suggested that carboxylate groups are bidentate asymmetric bridging ligands.

Key words: 4-methoxy-2-methylbenzoic acid, DTA, IR spectra, magnetic moments, synthesis, TG

4-Methoxy-2-methylbenzoic acid, $C_6H_3(CH_3)(OCH_3)COOH$, known as methylanisic acid, is a crystalline solid, sparingly soluble in water [1,2]. Its complexes of metal ions are little known. 4-Methoxy-2-methylbenzoates of Y(III) and lanthanide(III) [3] were prepared as crystal solids with general formula $LnL_3 \cdot nH_2O$, where n = 1, 0. Monohydrates heated in air lose the crystallization water and the anhydrous complexes decompose to oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7. Only the La(III) complex decomposes to oxide with intermediate formation of $La_2O_2CO_3$. The carboxylate groups in the studied complexes are tridentate chelating-bridging or bidentate chelating.

The aim of our work was to prepare the complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 4-methoxy-2-methylbenzoic acid in solid state and to study their properties and thermal decomposition in air.

EXPERIMENTAL

The complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 4-methoxy-2-methylbenzoic acid were prepared by dissolving freshly precipitated metal(II) carbonates in hot 0.1 M solution of 4-methoxy-2-methylbenzoic acid and crystallization at room temperature. The precipitate formed was filtered off, washed with hot water and dried at 303 K to a constant mass. The carbon and hydrogen contents in the prepared complexes were determined by elemental analysis on a Perkin Elmer CHN 2400 analyser. The contents of metal were determined by AAS method using an atomic absorption spectrophotometer AAS–3 (Carl Zeiss, Jena). The number of crystallization water molecules was determined from TG curve and by heating of the hydrated complexes at fixed temperature. The experimental results of these analysis confirm the calculated data. The IR spectra of the prepared 4-methoxy-2-methylbenzoates, and spectra of free 4-methoxy-2-methylbenzoic acid and its sodium salt were recorded as KBr discs on a Specord M-80 spectrophotometer (4000–400 cm^{-1}). The powder diffractograms of the prepared complexes and the products of their thermal decomposition were recorded by Debye-Scherrer powder method using CuK_α radiation and X-ray diffractometer HZG 4 AZ. The measurements were made over the range $2\Theta = 5–80°$. The magnetic susceptibility of the prepared complexes was measured on a magnetic balance (Scherwood Scientific MSB MK) at 293 K using as a standard $Co[Hg(SCN)_4]$. The thermal stability of the prepared 4-methoxy-2-methylbenzoates was investigated in air atmosphere. Measurements were made with θ-1500 D derivatograph with Derill converter with a sensitivity of 100 mg (TG). The sensitivity of DTA and DTG curves were regulated by Derill computer program. Samples of 100 mg were heated in air in platinum crucibles to 1273 K at a heating rate 10 K min^{-1} with a full scale. The hydrated complexes were heated isothermally at a set temperature to a constant mass. The products of dehydration and decomposition were confirmed by IR spectra and X-ray diffractograms.

RESULTS AND DISCUSSION

4-Methoxy-2-methylbenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared as solids with colour characteristic for hydrated metal(II) ions and with general formula $M(C_9H_9O_3)_2\cdot nH_2O$, where n = 1 for Mn, Co, Ni, Cu, n = 0 for Zn and n = 2 for Cd. The complexes prepared are crystalline solids of low symmetry and different structure. They are soluble in water. Their solubility is of the order 10^{-2}–10^{-3} mole dm^{-3} (Table 1) changing in the sequence:

$Cu << Cd < Zn << Co = Ni < Mn$

The IR spectra of the complexes prepared are similar to each other and exhibit many bands (Table 1). When the acid is converted to the M(II) complex, the stretching vibrations of C=O, ν(CO) in COOH group at 1680 disappear and the bands of asymmetrical (ν_{as}) and symmetrical (ν_s) vibrations of OCO group appear at 1610 cm^{-1} and 1392–1400 cm^{-1}, respectively, the bands of OCH_3 with max. at 1392–1388, 1288–1284 and 1248 cm^{-1}, the bands of CH_3 at 2980 and 2850, 1480–1472, 1336–1326, 1264 cm^{-1} and the bands of the M–O bond at 600–570 cm^{-1}. In the IR spectra of the prepared 4-methoxy-2-methylbenzoates are numerous bands of aromatic benzene ring at 1168–1160, 1104–1096, 1048 and 920 cm^{-1}, and the bands at 840–836 and 788–780 cm^{-1} [4–10].

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

Complex	ν(OH)	$\nu_{as}(OCO)$	$\nu_s(OCO)$	$\nu_{as} - \nu_s$	ν(M–O)	$\mu_{eff.}$(B.M.)	Solubility 10^{-3} mol dm^{-3}
$MnL_2^*\cdot H_2O$	3450	1610	1395	215	570	5.65	36.50
$CoL_2\cdot H_2O$	3400	1610	1395	215	580	4.69	15.0
$NiL_2\cdot H_2O$	3450	1610	1400	210	580	3.18	15.0
$CuL_2\cdot H_2O$	3400	1610	1395	215	580	1.27	0.87
ZnL_2	–	1610	1400	210	590	–	6.70
$CdL_2\cdot 2H_2O$	3350	1610	1400	210	600	–	4.29
$NaL\cdot xH_2O$	3400	1516	1392	124	–	–	–

$L^* – [C_6H_3(CH_3)(OCH_3)COO]^-$

These bands are shifted insignificantly (8–5 cm^{-1}) or do not change their position compared to the respective bands of 4-methoxy-2-methylbenzoic acid. This indicates that metal(II) ions have only a weak influence on the benzene ring. The frequencies of M–O bond for complexes studied increases with increasing of atomic number Z from 570 cm^{-1} for Mn(II) complex to 600 cm^{-1} for Cd(II) one (Table 1). The separation value ($\Delta\nu$) of ν_{as}(OCO) and ν_s(OCO) in the IR spectra of the prepared complexes (($\Delta\nu$) = 210–215 cm^{-1}) are greater than for the sodium salt, what permits to suggest a great degree of ionic bond. The bands of asymmetrical vibrations (ν_{as}) are significantly shifted to higher frequencies (94 cm^{-1}) and the bands of symmetrical vibrations (ν_s) insignificantly (3–8 cm^{-1}) to higher frequencies compared to those bands for the sodium salt. From the shifts of ν_{as}(OCO) and ν_s(OCO) in the IR spectra of the complexes prepared compared to the respective bands of sodium salt, the spectroscopic criteria [6–8] and the previous works [11–13], it can be suggested that the OCO groups are bonded probably as bidentate asymmetrical bridging ligands and the complexes exist probably as dimers. In the complexes of Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) there are broad absorption bands of ν(OH) with max. at 3450–3350 cm^{-1} characteristic for hydrates.

The complexes prepared are stable in air. When heated in air, they are decompose in various ways (Table 2). The hydrated complexes of Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) are stable up to 323–373 K, whereas anhydrous Zn complex up to 493 K.

Table 2. Data for dehydration and decomposition of 4-methoxy-2-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)
		Calc.	Found.			Calc.	Found.	
$MnL^* \cdot H_2O$	373–425	4.47	4.5	1	525–778	76.59	76.5	778
$CoL \cdot H_2O$	323–454	4.42	4.4	1	478–873	75.86	76.6	873
$NiL \cdot H_2O$	323–423	4.42	4.4	1	453–823	76.36	76.0	823
$CuL \cdot H_2O$	353–397	4.37	4.4	1	415–953	79.78	80.1	953
ZnL	–	–	–	–	493–923	79.42	79.5	923
CdL	–	–	–	–	443–756	65.64	65.6	756

$^*L = [C_6H_3(CH_3)(OCH_3)COO]^-$

ΔT_1 – temperature range of dehydration

ΔT_2 – temperature range of decomposition

T_k – temperature over which the oxides exist

The thermal stability of the prepared complexes increases in the order:

Co = Ni < Cu < Cd < Mn << Zn

The hydrated complexes lose crystallization water molecules in one step over the range 323–454 K. The anhydrous complexes are stable up to 415–493 K (Mn complex up to 525 K) and next the complexes of Cu, Zn and Cd decompose directly to oxides CuO, ZnO and CdO, whereas the complexes of Mn, Co and Ni decompose to oxides Mn_3O_4, Co_3O_4, NiO with intermediate formation of mixture of free metals and their oxides. The dehydration process is endothermic, whereas the combustion of organic ligand, products of decomposition and oxidation of free metal to its oxide proceed with strong exothermic effects. The temperatures, over which oxides are formed, change from 746 K for Cd complex, to 953 K for Cu one, and increase in the order:

Cd < Mn < Ni < Co < Zn < Cu

The results suggest following schemes of thermal decomposition of M(II) 4-methoxy-2-methylbenzoates:

$ML_2{\cdot}H_2O \rightarrow ML_2 \rightarrow M + M_3O_4 \rightarrow M_3O_4$, M = Mn, Co, $NiL_2{\cdot}H_2O \rightarrow NiL_2 \rightarrow Ni + NiO \rightarrow NiO$, $ML_2{\cdot}nH_2O \rightarrow ML_2 \rightarrow MO$, M = Cu, Cd, $ZnL_2 \rightarrow ZnO$

The complexes of Zn and Cd are diamagnetic. The susceptibility values for paramagnetic Mn(II), Co(II), Ni(II) and Cu(II) complexes, calculated from magnetic measurements at 293 K, were corrected by measuring the diamagnetic susceptibility of the ligand. The effective magnetic moments were calculated using the formula $\mu_{eff} = 2.84\,(X_MT)^{1/2}$ (Table 2) and they are for the complexes of Ni (3.18 B.M.) and Mn (5.65 B.M.) similar to the theoretical values for the octahedral complexes with configuration d^8 and d^5, respectively [14]. The value μ_{eff} for Mn(II) complex (5.65 B.M.) shows on the high spin configuration (μ_{eff} = 5.6–6.1 B.M.) and octahedral structure [14]. For Co(II) complex the measured magnetic moment (4.96 B.M.) differs from the spin-only value. Its magnetic moment, instead of spin-only 3.88 B.M. characteristic for d^7 configuration (three unpaired electrons), attains value 4.95 B.M. Literature data [4,14] show that measured magnetic moments for Co(II) complexes with different ligands attain value up to 5.2–5.5 B.M. The effective magnetic moment (1.27 B.M.) for Cu(II) complex is smaller than that calculated theoretically (spin-only 1.73 B.M. for d^9 configuration), what permits to suggest the Cu – Cu action.

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