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SPECTRAL, THERMAL AND MAGNETIC INVESTIGATIONS OF Mn(II), Co(II), Ni(II), Cu(II), Zn(II) AND Cd(II) 4-METHYLPHTHALATES

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Abstract

Conditions for the preparation of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 4-methylphthalates were investigated and their composition, solubility in water at 295 K and magnetic moments were determined. IR spectra and powder diffraction patterns of the complexes prepared with molar ratio of metal to organic ligand of 1.0:1.0 and general formula: M $[CH_3C_6H_3(CO_2)_2]\cdot nH_2O$ (n=1–3) were recorded and their decomposition in air were studied. During heating the hydrated complexes are dehydrated in one (Mn, Co, Ni, Zn, Cd) or two steps (Cu) and next the anhydrous complexes decompose to oxides directly (Cu, Zn), with intermediate formation of carbonates (Mn, Cd), oxocarbonates (Ni) or carbonate and free metal (Co). The carboxylate groups in the complexes studied are mono- and bidentate (Co, Ni), bidentate chelating and bridging (Zn) or bidentate chelating (Mn, Cu, Cd). The magnetic moments for paramagnetic complexes of Mn(II), Co(II), Ni(II) and Cu(II) attain values 5.92, 5.05, 3.36 and 1.96 M.B., respectively.

Keywords: IR spectra, magnetic moments, 4-methylphthalate, thermal analysis

Introduction

4-Methylphthalic acid is a crystalline solid soluble in water (especially in hot water), ethanol, ethyl acetate and acetone and insoluble in benzene and $CHCl_3$ [1]. The rare earth element 4-methylphthalates were prepared as solids with general formula $Ln_2[CH_3C_6H_3(COO)_2]_3\cdot nH_2O$ [2]. The COO^- groups in these complexes act as bidentate chelating and bidentate bridging. During heating the hydrated complexes are dehydrated in one or two steps and next decompose to the oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7. The solid state complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 4-methylphthalic acid have not been studied so far. Nair and Parthasarathy [3, 4] have determined the thermodynamic stability constants and the dissociation constants of the 1.0:1.0 complexes of these elements with 4-methylphthalic acid.

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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-methylphthalic acid in solid state and to examine their properties.

Experimental

4-Methylphthalates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared by dissolving freshly precipitated carbonates of M(II) ions in hot 0.1 M solution of 4-methylphthalic acid (the complex of Zn(II) was prepared from ZnO) and after filtration of an excess of carbonate or oxide ZnO their crystallization at room temperature. The precipitates formed were filtered off, washed with water and dried at 303 K to a constant mass. The contents of carbon and hydrogen were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser. The content of metal ions in the complexes was determined by transforming the complexes into oxides and from the TG curves. The content of the crystallization water was determined from the TG curves and by isothermal heating of the hydrated complexes. The solubility of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes in water at 295 K were determined by measuring the concentration of M(II) ions in saturated (under isothermal conditions) solution using AAS method on an atomic absorption spectrophotometer AAS-3 (Carl-Zeiss, Jena). The IR spectra of 4-methylphthalic acid, its M(II) complexes and sodium salt were recorded as KBr discs on a SPECORD M-80 spectrophotometer over the range 4000–400 cm^{-1}. X-ray diffractograms of the prepared complexes were recorded using diffractometer HZG 4 A2. The thermal stabilities of the prepared 4-methylphthalates were investigated by TG, DTG and DTA curves using Q-1500D derivatograph at a heating rate of 10 K min^{-1}. The samples (100 mg) were heated in air in platinum crucibles to 1273 K. The DTG and DTA sensitivities are regulated by MOM Derill program. Al_2O_3 was used as a standard. Moreover, the process of dehydration was studied using Setsys 16/18 (SETARAM) derivatograph, samples were heated to 573 K at a heating rate of 2.5 K min^{-1}. The magnetic susceptibility of the prepared complexes was measured at room temperature by Gouy's method on a magnetic balance (Sherwood Scientific MSB MK I) using a standard $Co[Hg(SCN)_4]$.

Results and discussion

4-Methylphthalates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared as solids with a colour characteristic for M(II) ions and as complexes of a 1.0:1.0 molar ratio of metal to organic ligand, with a general formula $M[CH_3C_6H_3(COO)_2]\cdot nH_2O$, where n=1–3 (Table 1). The prepared complexes (except of Co(II) and Ni(II) complexes) are crystalline solids of different structures (Fig. 1). All the complexes are soluble in water (Table 1). The solubility are of the order 10^{-3}–10^{-1} mol dm^{-3}. 4-Methylphthalates of Ni(II) and Co(II) are the best soluble ($2.0\cdot10^{-1}$ and $3.7\cdot10^{-1}$ mol dm^{-3}), whereas those of Cu(II)

Table 1 Analytical data and solubility in water (at 295 K) of 4-methylphthalates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

Complex	M/%		C/%		H/%		Solubility/ mol dm^{-3}·10^{-2}
	calcd.	found	calcd.	found	calcd.	found	
$Mn[CH_3C_6H_3(COO)_2]\cdot H_2O$	21.88	21.5	43.05	43.2	3.21	3.1	7.43
$Co[CH_3C_6H_3(COO)_2]\cdot 3H_2O$	20.24	20.6	37.13	37.3	4.15	4.0	20.19
$Ni[CH_3C_6H_3(COO)_2]\cdot 3H_2O$	20.18	20.0	37.16	37.2	4.19	4.3	37.30
$Cu[CH_3C_6H_3(COO)_2]\cdot 2H_2O$	22.88	22.9	38.92	38.6	3.63	3.4	0.52
$Zn[CH_3C_6H_3(COO)_2]\cdot 1.5H_2O$	24.16	24.1	39.95	39.6	3.35	3.2	2.84
$Cd[CH_3C_6H_3(COO)_2]\cdot H_2O$	36.42	36.5	35.03	35.2	2.94	2.5	0.23

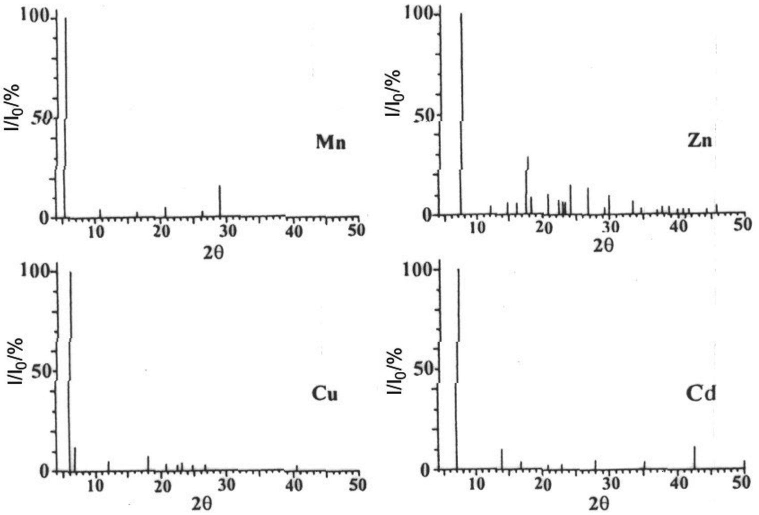

Fig. 1 X-ray diffraction sheet of Mn(II), Cu(II), Zn(II) and Cd(II) 4-methylphthalates

and Cd(II) are the least soluble ($5.2\cdot10^{-3}$ and $2.3\cdot10^{-3}$ mol dm^{-3}). The solubility of prepared complexes decrease in the sequence:

$$Ni>Co>>Mn>Zn>>Cu>Cd$$

Table 2 Magnetic moments of 4-methylphthalate of Mn(II), Co(II), Ni(II) and Cu(II) at 295 K

Central atom	n	μ_{eff} found/ M.B.	μ_{eff} spin-only/ M.B.	Experimental values of μ_{eff} [5]/ M.B.
Mn^{2+}	5	5.92	5.92	5.6–6.1
Co^{2+}	7	5.05	3.88	4.3–5.2
Ni^{2+}	8	3.36	2.83	2.8–3.5
Cu^{2+}	9	1.96	1.73	1.7–2.2

The susceptibility values for paramagnetic Mn(II), Co(II), Ni(II) and Cu(II) complexes calculated from the results of magnetic measurements at room temperature were corrected by measuring the diamagnetic susceptibility of ligand. The magnetic moments were calculated using formula $\mu_{eff}=2.84(\chi_{M}T)^{1/2}$ (Table 2). The complexes of Zn(II) and Cd(II) were diamagnetic. The magnetic moments determined for the complexes of Mn(II) (5.92 M.B.) and Cu(II) (1.96 M.B.) are similar to the theoretical values for octahedral complexes with configuration d^5 and d^9, respectively. The value of μ_{eff} for Mn(II) complex shows on the high spin configuration and octahedral structure [5]. For Co(II) and Ni(II) complexes the measured magnetic moments differ to such from the spin-only moments. The magnetic moment for Co(II) complex instead of spin-only value 3.88 M.B. characteristic for d^7 configuration (three unpaired electrons) attains value 5.05 M.B. Alike the magnetic moment for Ni(II) instead of value 2.83 M.B. characteristic for d^8 configuration (two unpaired electrons) attains value 3.36 M.B. Literature data show that measured magnetic moments for Co(II) (high spin configuration) and Ni(II) complexes with different ligands attain values 4.3–5.2 M.B. and 2.8–3.5 M.B., respectively [5]. The value of μ_{eff} for Co(II) and Ni(II) complexes are in this range, what suggests an octahedral structure of 4-methylphthalates of Co(II) and Ni(II).

Table 3 Frequencies of maximum of absorption bands in IR spectra of 4-methylphthalates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Na(I) (cm^{-1})

Complex	ν_{as}(COO)	$\Delta\nu_{as}^{*}$	ν_{s}(COO)	$\Delta\nu_{s}^{*}$	ν_{as}–ν_{s}	ν(M–O)
$MnL\cdot H_2O$	1552	0	1420	12	132	440
$CoL\cdot 3H_2O$	1552	0	1408	0	144	440
$NiL\cdot 3H_2O$	1552	0	1408	0	144	440
$CuL\cdot 2H_2O$	1536	–16	1416	8	120	456
$ZnL\cdot 1.5H_2O$	1560, 1536	8–16	1428	20	132, 108	448
$CdL\cdot H_2O$	1548	–4	1428	20	120	432
Na_2L	1552	–	1408	–	144	–

L – $4\text{-}CH_3C_6H_3\text{-}1,2\text{-}(COO)_2^{2-}$; *Shifts of absorption bands ν_{as}(COO) and ν_{s}(COO) compared with bands of sodium 4-methylphthalate

The 4-methylphthalic acid exhibits a strong absorption band at 1692 cm^{-1} of C=O in COOH. In the IR spectra of the complexes prepared, the band of COOH group disappears while the bands of asymmetrical vibrations ν_{as}(COO) at 1560–1536 cm^{-1} and the bands of symmetrical vibrations ν_{s}(COO) at 1428–1408 cm^{-1} appear (Table 3). There are also absorption band of ν(OH) of the water with max. 3440–3368 cm^{-1} and the absorption band of the M–O bond at 456/432 cm^{-1}. The separation value (ν_{as}–ν_{s}) of the COO^{-} groups and the direction of the shift of these bands, when compared to sodium salt, may suggest, that COO^{-} groups occurs as mono- and bidentate in the investigated complexes [6, 7]. In the IR spectra of Co(II) and Ni(II) complexes the bands ν_{as}(COO) and ν_{s}(COO) appear at 1552 cm^{-1} and 1408 cm^{-1} and are the same as for the sodium salt. On this basis, it is possible to suggest, that the carboxylate groups act as mono- and bidentate groups and that the degree of ionic bond in these complexes is the same as in sodium salt. Co(II) and Ni(II) ions have probably CN=6, similarly as in [8–10]. In the IR spectrum of Zn(II) complex the separation value (ν_{as}–ν_{s}) of the COO^{-} groups is smaller than for the sodium salt, the band ν_{as}(COO) is splitted (1560 and 1536 cm^{-1}) and the band of symmetrical vibration ν_{s}(COO) is shifted to higher frequencies compared to sodium salt, what suggests, that the COO^{-} groups are bonded in different ways. Probably the carboxylate groups act as bidentate chelating and bridging groups. The presence 1.5 H_2O molecules suggest that the Zn(II) complex form dimer. Literature data show, that carboxylates of Zn(II) form dimeric structure [11]. The ν_{as}(COO) bands for the Cu(II) and Cd(II) complexes are shifted to lower frequencies and ν_{s}(COO) bands to higher ones, compared to the sodium salt, what suggest, that the carboxylate groups act as bidentate symmetrical

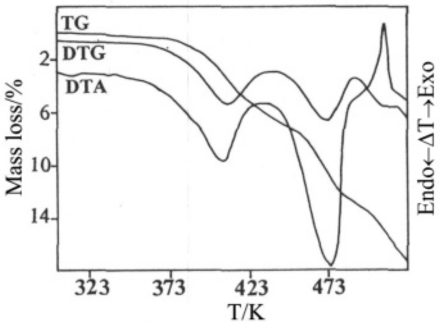

Fig. 2 TG, DTG and DTA curves of dehydration of $ZnC_9H_6O_4\cdot1.5H_2O$

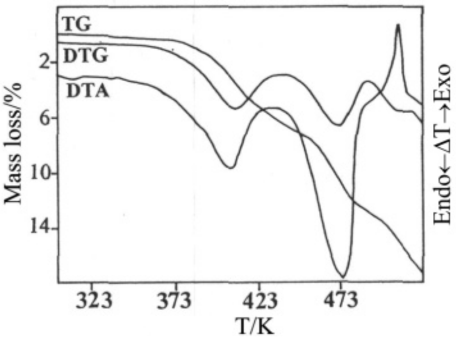

Fig. 3 TG, DTG and DTA curves of dehydration of $CuC_9H_6O_4\cdot2H_2O$

chelating. With regard for steric structure it is possible, that these complexes form dimers $Cu_2L_2\cdot4H_2O$ and $Cd_2L_2\cdot2H_2O$. The Cu(II) complexes with carboxylic acids often form dimeric structure [8]. The band of asymmetric vibration $\nu_{as}(COO)$ for 4-methylphthalate of Mn(II) is the same value, compared to band of sodium salt and the band of symmetrical vibration $\nu_s(COO)$ is shifted to higher frequencies. On this basis, it is possible to suggest, that, in the discussed complex, the carboxylate groups act as bidentate asymmetrical chelating.

The complexes prepared are stable at room temperature. During heating they decompose in different ways (Table 4). The hydrated complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are stable up to 325–398 K and then they lose some water molecules in one (Mn, Co, Ni, Zn, Cd) (Fig. 2) or two steps (Cu) (Fig. 3) over the range 484–560 K. The dehydration process in connected with endothermic effect at 378–478 K (for Cu at 405 and 474 K). Next the anhydrous complexes decompose in different ways. The 4-methylphthalates of Cu(II), Zn(II) and Cd(II) are, probably, dimers. Complex of Cu(II) lose water molecules in two steps. In the complexes of Zn(II) and Cd(II) the water molecules are, probably in the inner sphere and the complexes have formula $[Zn_2L_2\cdot3H_2O]$ and $[Cd_2L_2\cdot2H_2O]$, respectively. The anhydrous complexes Mn(II), Zn(II) and Cd(II) are stable up to 588–641 K and then decompose to oxides over the range 835–1049 K. 4-Methylphthalates of Mn(II) and Cd(II) decompose to oxides with intermediate formation of carbonates at 761 and 670 K, re-

Table 4 Thermal data dehydration and decomposition of 4-methylphthalates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) in air atmosphere

Complex	T_{dehydr} range/K	Loss of mass/%		T_{endo} DTA/ K	H_2O loss/*n*	T_c/K	Loss of mass/%		T_{decomp}/K	Loss of mass/%		T_K/K
		calcd.	found				calcd.	found		calcd.	found	
MnL·H_2O	367–488	7.17	7.0	417	1	761	54.20	54.5	641–1049	69.63	68.9	$1049^{\bullet}$
CoL·$3H_2O$	325–560	18.57	18.9	378	3	718	59.15	59.2	560–1195	74.26	73.8	840* 875** 1195***
NiL·$3H_2O$	325–553	18.58	18.3	378	3	666–699	66.76	66.7	553–785	74.32	74.5	785°
CuL·$2H_2O$	351–440 440–496	6.48 12.97	6.6 12.5	405 474	1 2	–	–	–	496–785	71.36	71.6	785°
ZnL·$1.5H_2O$	398–484	9.99	10.0	450	1.5	–	–	–	603–962	69.93	69.6	962°
CdL·H_2O	381–502	5.84	6.0	478	1	670	44.13	44.7	588–835	58.39	58.3	835°

L – 4-$CH_3C_6H_3$-1,2-$(COO)_2^{2-}$
T_{dehydr} – temperature of dehydration
T_{decomp} – temperature of decomposition
T_c – temperature of carbonate and Ni_2OCO_3 formation
T_K – temperature over forms $^{\bullet}Mn_3O_4$, *Co, **Co_3O_4, ***CoO, ^{o}NiO, CuO, ZnO and CdO

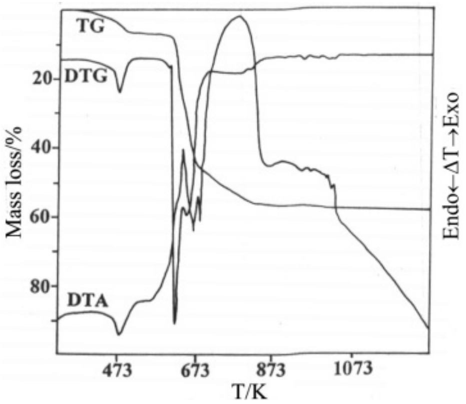

Fig. 4 TG, DTG and DTA curves of $CdC_9H_6O_4\cdot H_2O$

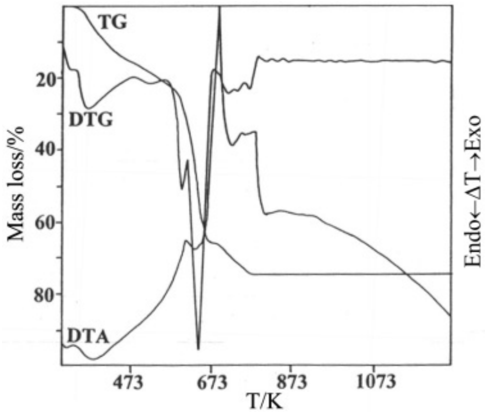

Fig. 5 TG, DTG and DTA curves of $NiC_9H_6O_4\cdot 3H_2O$

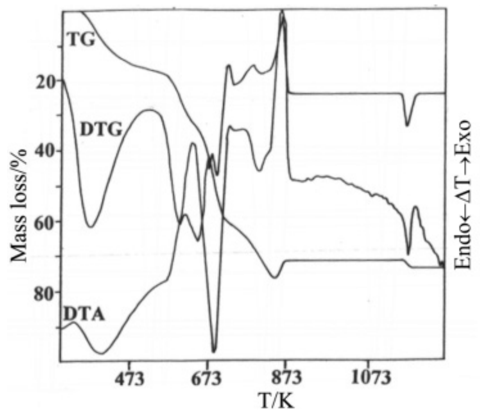

Fig. 6 TG, DTG and DTA curves of $CoC_9H_6O_4\cdot 3H_2O$

spectively (Fig. 4). The anhydrous complexes Co(II), Ni(II) and Cu(II) are not stable and decompose directly in different ways to the oxides CoO, NiO and CuO. 4-Methylphthalate of Ni(II) decompose with intermediate formation of oxocarbonate $NiO \cdot NiCO_3$ (stable at 666–699 K) (Fig. 5). The complex of Co(II) decompose through carbonate $CoCO_3$ (718 K) to free metal (840 K) and next is oxidized to Co_3O_4 stable at 875–1065 K. The final product of decomposition is CoO, which is formed over 1195 K (Fig. 6). The results suggests the following scheme of the thermal decomposition of M(II) 4-methylphthalates:

$$MnL \cdot H_2O \to MnL \to MnCO_3 \to Mn_3O_4$$

$$ZnL \cdot 1.5H_2O \to ZnL \to ZnO$$

$$CdL \cdot H_2O \to CdL \to CdCO_3 \to CdO$$

$$CoL \cdot 3H_2O \to CoL \to CoCO_3 \to Co \to Co_3O_4 \to CoO$$

$$NiL \cdot 3H_2O \to NiL \to Ni_2OCO_3 \to NiO$$

$$CuL \cdot 2H_2O \to CuL \to CuO$$

The hydrated complexes Co(II), Ni(II) and Cu(II) during heating lose crystallization water molecules and change their colour to that characteristic for anhydrous ions. The position of ν_{as} and $\nu_s COO^-$ groups of the hydrated and anhydrous complexes Co(II) and Ni(II) are the same, what indicates that structure of salts do not change (Table 5). From the results obtained, it is possible, that the complexes Co(II) and Ni(II) have a dimeric structure with formula $[M(H_2O)_6][ML_2]$. The one metal ion (Co, Ni) coordinate six water molecules forming cation $[M(H_2O)_6]^{2+}$ and two organic ligands are bonded with the second metal ion forming anion $[ML_2]^{2-}$. The similar types of structure were described for dichlorobenzoates of Co(II) and Ni(II) [8–10]. The values of ν_{as} and ν_s COO^- of the remaining hydrated and anhydrous complexes are different (Table 5), what suggests the different character of the bond between the organic ligand and the M(II) ions in hydrated and anhydrous salts.

Table 5 Frequencies of absorption bands of COO^- groups for 4-methylphthalates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) before and after dehydration (cm^{-1})

Complex	Before dehydration			After dehydration		
	$\nu_{as}(COO)$	$\nu_s(COO)$	colour	$\nu_{as}(COO)$	$\nu_s(COO)$	colour
$MnL \cdot H_2O$	1552	1420	pale pink	1552	1432	pale pink
$CoL \cdot 3H_2O$	1552	1408	dark pink	1552	1408	dark blue
$NiL \cdot 3H_2O$	1552	1408	green	1552	1408	yellow-green
$CuL \cdot 2H_2O$	1536	1416	blue	1600	1424	green
$ZnL \cdot 1.5H_2O$	1560, 1536	1428	white	1540	1428	white
$CdL \cdot H_2O$	1548	1428	white	1536	1412	white

L – $4\text{-}CH_3C_6H_3\text{-}1,2\text{-}(COO)_2^{2-}$

Conclusions

4-Methylphthalates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared as hydrates with molar ratio of metal to organic ligand of 1.0:1.0 and general formula $M(C_9H_6O_4)\cdot nH_2O$ where n=1–3 and with colour characteristic for hydrated M(II) ions. The prepared complexes (except of Co(II) and Ni(II) complexes) are crystalline solids of different structures. The complexes of Mn(II), Co(II), Ni(II) and Cu(II) are paramagnetic with magnetic moments equals 5.92, 5.05, 3.36 and 1.96 M.B., respectively. The complexes of Zn(II) and Cd(II) are diamagnetic. The complexes are soluble in water. Their solubility are of the order 10^{-1} to 10^{-3} mol dm^{-3}. The carboxylate groups in the studied complexes act as mono- and bidentate (Co, Ni), bidentate chelating and bridging (Zn) or chelating (Mn, Cu, Cd). The hydrated complexes are stable in air at room temperature. During heating they are decomposed in different ways. Hydrated 4-methylphthalates are dehydrated in one (Mn, Co, Ni, Zn, Cd) or two steps (Cu) and next decompose to oxides directly (Cu, Zn), with intermediate formation of carbonates (Mn, Cd), oxocarbonate (Ni) or carbonate and free metal (Co). Temperatures over which the oxides exist decrease in the order:

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

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