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NEW COMPLEXES OF Mn(II), Co(II), Ni(II), Cu(II), Zn(II) AND Cd(II) WITH 3,3-DIMETHYLGLUTARIC ACID

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Abstract

Conditions for the preparation of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 3,3-dimethylglutarates were investigated and their quantitative composition, solubility in water at 293 K and magnetic moments were determined. IR spectra and powder diffraction patterns of the complexes prepared with general formula $MC_7H_{10}O_4 \cdot nH_2O$ (n=0–2) were recorded and their thermal decomposition in air were studied. During heating the hydrated complexes of Mn(II), Co(II), Ni(II) and Cu(II) are dehydrated in one step and next all the anhydrous complexes decompose to oxides directly (Mn, Co, Zn) or with intermediate formation free metal (Ni, Cu) or oxocarbonates (Cd). The carboxylate groups in the complexes studied are bidentate. The magnetic moments for the paramagnetic complexes of Mn(II), Co(II), Ni(II) and Cu(II) attain values 5.62, 5.25, 2.91 and 1.41 M.B., respectively.

Keywords: 3,3-dimethylglutarate, DTA, IR spectra, magnetic moments, synthesis, TG

Introduction

3,3-Dimethylglutaric acid, $C_5H_{10}(COOH)_2$, is a crystalline solid soluble in water and ethanol [1]. It is used in the synthesis of (+) –bicyclohumelone, and important perfume component [2]. Compounds of 3,3-dimethyglutaric acid with metal ions are little known. The complex of La was prepared as solid sparingly soluble in water [3]. The complexes of Y(III) and lanthanides(III) from La to Lu [4] were prepared as solids with general formula $Ln_2C_7H_{10}O_4 \cdot nH_2O$, sparingly soluble in water. The complexes heated are dehydrated in one or three steps and next the anhydrous compounds decompose to oxides directly (Ce) or with intermediate formation $Ln_2O_2CO_3$ (Y, La, Pr–Lu). The carboxylate groups in the complexes are bidentate.

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 3,3-dimethylglutaric acid in solid state and to study their properties and thermal decomposition.

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Experimental

The complexes of Mn(II), Co(II), Ni(II) , Cu(II), Zn(II) and Cd(II) with 3,3-dimethylglutaric acid were prepared by dissolving metal(II) carbonates in hot 0.1 M solution of 3,3-dimethylglutaric acid and crystallization at room temperature. The precipitates formed were filtered off, washed with 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 on an atomic absorption spectrophotometer AAS – 3 (Carl Zeiss Jena). The number of crystallization water molecules was determined from TG curves and by isothermal heating the hydrated complexes at defined temperature (Table 3). IR spectra of the prepared complexes and spectra of 3,3-dimethylglutaric acid and its sodium salt were recorded as KBr discs on a Specord M-80 spectrophotometer (4000–400 cm^{-1}). The solubility of the prepared complexes in water at 293 K was determined by the preparation of saturated solutions (under isothermal conditions) and measuring the concentration of metal(II) ions using AAS method. The powder diffraction patterns of the prepared 3,3-dimethylglutarates are registered on a Dron-2 diffractometer. The magnetic susceptibility of the prepared complexes was measured at room temperature by Gouy's method on a magnetic balance (Scherwood Scientific MSB MK I) using as standard $Co[Hg(SCN)_4]$ (Table 2). Thermal stability of the prepared 3,3-dimethylglutarates was investigated by TG, DTG and DTA curves. Measurements were made with Q-1500 D derivatograph by method described in [4]. The products of decomposition were calculated from TG curves and verified by registration X-ray diffractograms and IR spectra.

Results and discussion

3,3-Dimethylglutarates 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 with general formula $M(C_5H_{10}C_2O_4)\cdot nH_2O$, where n=0 for Zn, Cd, n=1 for Ni, n=1.5 for Co, and n=2 for Cu (Table 1). The prepared complexes are crystalline solids of different structures (Fig. 1). All the prepared complexes, except for Cu(II) complex, are soluble in water (Table 1). Their solubility is of the order 10^{-2} mol dm^{-3}, whereas the solubility of Cu(II) one is $2.4\cdot10^{-3}$ mol dm^{-3}. The solubility of the prepared complexes change in the order:

$$MnL > NiL > CdL > CoL > ZnL >> CuL$$

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 Ni(II) (2.91 M.B.) and Mn(II) (5.62 M.B.) are similar to the theoretical values for octahedral complexes with configuration d^8 and d^5, respectively. The value μ_{eff} for Mn(II) complex shows on the high spin configuration (μ_{eff}= 5.9–6.2 M.B. [5]) and octahedral structure. For Co(II) complex the measured magnetic moment (5.25 M.B.) differs to such an extent from the spin-only moment. Its magnetic moment, instead of spin – only value 3.88 M.B. characteristic for d^7 configuration (three unpaired electrons) attains value 5.25 M.B. Literature data [6] show that measured magnetic moments for Co(II) complexes with different ligands attain value 5.2–5.5 M.B. The magnetic moment value (1.40 M.B.) for Cu(II) complex shows on the polymeric structure.

Table 1 Analytical data and solubilities of 3,3-dimethylglutarates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

Complex	M/%		C/%		H/%		Solubility/ 10^{-2} mol dm^{-3}
	calc.	found	calc.	found	calc.	found	
$Mn[C_5H_{10}(COO)_2]\cdot 2H_2O$	22.07	22.00	33.74	33.52	5.60	5.61	3.84
$Co[C_5H_{10}(COO)_2]\cdot 1.5H_2O$	24.16	24.10	34.43	33.98	5.32	5.42	1.63
$Ni[C_5H_{10}(COO)_2]\cdot H_2O$	24.59	24.60	35.19	35.31	5.03	5.07	3.40
$Cu[C_5H_{10}(COO)_2]\cdot H_2O$	26.52	26.50	34.43	34.33	5.00	4.95	0.24
$Zn[C_5H_{10}(COO)_2]$	29.28	29.25	37.60	37.50	4.47	4.40	1.03
$Cd[C_5H_{10}(COO)_2]$	41.56	41.55	31.06	31.00	3.69	3.70	2.10

All the prepared complexes exhibit similar solid state IR spectra (Table 2). When the acid is converted to the complex, the stretching vibrations of C=O group, ν(C=)O in COOH group at 1715 and 1680 cm^{-1} disappear, whereas the band of asymmetric vibrations ν_{as}(OCO) at 1552–1608 cm^{-1} and the bands of symmetric vibrations

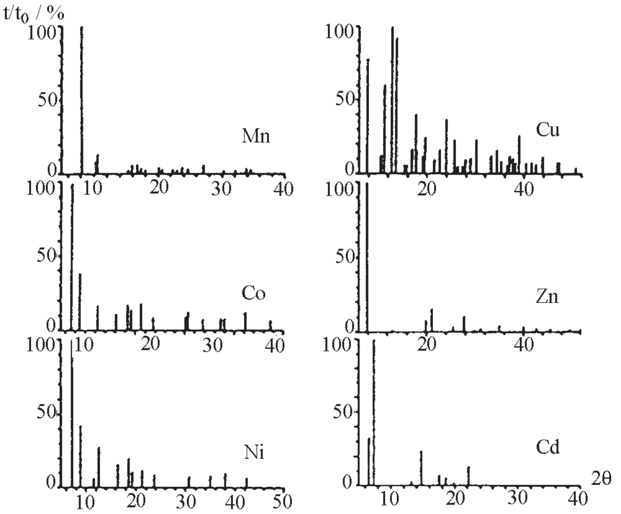

Fig. 1 Radiogram sheet of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 3,3-dimethylglutarates

at 1390–1450 cm^{-1} appear. In the IR spectra of the Mn(II), Co(II), Ni(II) and Cu(II) 3,3-dimethylglutarates there are broad absorption bands of ν(OH) with max. at 3416–3430 cm^{-1} and narrow bands of $\delta(H_2O)$ at 1610–1630 cm^{-1} confirming the presence of water molecules. The bands of metal–oxygen bond is observed at 500–550 cm^{-1}. The splitting for absorption bands of valency vibrations ν_{as}(OCO) and ν_s(OCO) ($\Delta\nu=\nu_{as}-\nu_s$) have values 156–176 cm^{-1} (for Cu(II) – 200 cm^{-1}) and are greater than for the sodium salt ($\Delta\nu$=126 cm^{-1}). On the basis of Δν value and previous work [7–9] it is possible to suggest that carboxylate groups in the complexes of Mn(II), Co(II) and Ni(II) act as bidentate chelating, whereas in the complexes of Cu(II), Zn(II) and Cd(II) as bidentate bridging and water molecules are in inner

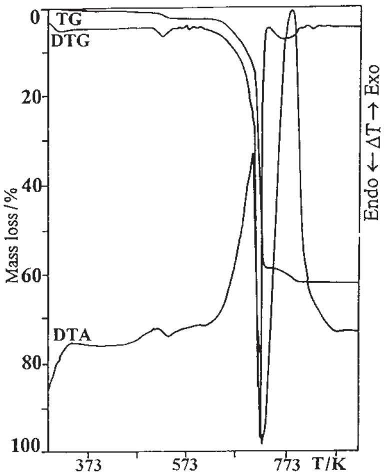

Fig. 2 TG, DTG and DTA curves of $ZnC_7H_{10}O_4$

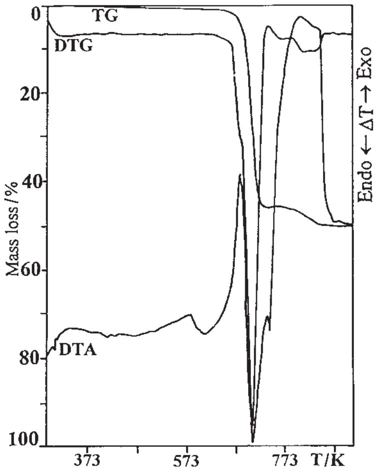

Fig. 3 TG, DTG and DTA curves of $CdC_7H_{10}O_4$

sphere of the complexes. Cu(II) ion has probably CN=5, similarly as in [7, 8] whereas Co(II), Ni(II) and Mn(II) ions have CN=6, which confirm magnetic measurements, whereas in the anhydrous complexes of Zn(II) and Cd(II) CN=4. In the Co(II) and Ni(II) complexes the water molecules act as bidentate ligand.

Table 2 Frequencies of characteristic absorption bands in IR spectra and magnetic moment (M.B.) of 3,3-dimethylglutarates of Mn(II), Co(II), Cu(II), Zn(II), Cd(II) and Ni(II) (cm^{-1})

Complex	N(OH)	ν_{as}(OCO)	ν_s(OCO)	ν_{as}–ν_s	ν(M–O)	μ_{eff} (M.B.)	*n*
$MnL^{*}\cdot 2H_2O$	3420	1552	1390	162	520	5.62	5
$CoL\cdot 1.5H_2O$	3420	1564	1408	156	540	5.25	3
$NiL\cdot H_2O$	3416	1568	1408	160	550	2.91	2
$CuL\cdot H_2O$	3430	1608	1408	200	525	1.40	1
ZnL	–	1590	1424	166	525	–	–
CdL	–	1584	1408	176	530	–	–
$Na_2L\cdot xH_2O$	3420	1576	1450	126	500	–	–

L^{*} – $C_5H_{10}(COO)_2^{2-}$; *n* – number of unpaired electrons

The prepared 3,3-dimethylglutarates are stable at room temperature and can be stored by for several months without change. During heating they decompose in different ways. Hydrated complexes of Mn(II), Co(II), Ni(II) and Cu(II) heated are stable up to 318–373 K, whereas anhydrous complexes of Zn(II) and Cd(II) up to 573 and 623 K, respectively. The thermal stability of the prepared complexes increases in the order:

$$NiL < CoL < MnL < CuL < Zn < CdL.$$

Anhydrous complex of Zn(II) heated decomposes to ZnO in the temperature range 573–793 K (Table 3, Fig. 2), whereas this of Cd(II) (Fig. 3) decomposes to CdO with intermediate formation oxocarbonate $CdO\cdot CdCO_3$. Dihydrated Mn(II) 3,3-dimethylglutarate heated loses two water molecules (333–433 K) and then anhydrous compound decomposes to Mn_3O_4 (513–763 K). Strong exothermic effect is connected with combustion of organic ligand. Hydrated Co(II) and Ni(II) complexes are dehydrated in one step. The anhydrous complex of Co(II) decomposes to free metal in the temperature range 493–753 K and next oxidizes to Co_3O_4. Anhydrous Ni(II) 3,3-dimethylglutarate decomposes directly to NiO in the range 463–743 K. Monohydrated Cu(II) complex loses water molecule in the range 373–473 K and next during heating decomposes to free metal, which oxidizes to CuO (633–743 K) (Fig. 4).The dehydration process is connected with the strong endothermic effect, whereas the combustion of organic ligand and oxidation of free metal to oxide with exothermic one.

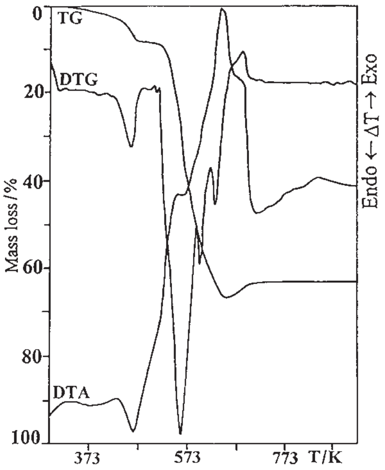

Fig. 4 TG, DTG and DTA curves of $CuC_7H_{10}O_4 \cdot H_2O$

Table 3 Data for dehydration and decomoposition of 3,3-dimethylglutarates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

Complex	ΔT_1/K	Mass loss/%		Loss of	ΔT_2/K	Mass loss/%		T_k/K
		calc.	found	H_2O/mol		calc.	found	
$MnL^* \cdot 2H_2O$	333–433	14.46	14.50	2	513–783	57.04	57.00	783
$CoL \cdot 1{,}5H_2O$	318–413	11.06	11.05	1.5	493–773	50.56	50.60	775
$NiL \cdot H_2O$	318–393	7.58	7.58	1	463–743	66.15	66.20	743
$CuL \cdot H_2O$	373–473	7.50	7.55	1	523–743	59.28	59.00	743
ZnL	–	–	–	–	573–793	63.57	63.50	793
CdL	–	–	–	–	623–853	52.51	52.50	853

L^* – $C_5H_{10}(COO)_2^{2-}$
ΔT_1 – temperature range of dehydration
ΔT_2 – temperature range of decomposition
T_k – temperature over which the oxides exist

The results suggest the following schemes of the thermal decomposition of M(II) 3,3-dimethylglutarates:

$$MnL \cdot 2H_2O \rightarrow MnL \rightarrow Mn_3O_4$$
$$CoL \cdot 1.5H_2O \rightarrow CoL \rightarrow Co \rightarrow Co_3O_4$$
$$NiL \cdot H_2O \rightarrow NiL \rightarrow NiO$$
$$CuL \cdot H_2O \rightarrow CuL \rightarrow Cu \rightarrow CuO$$
$$ZnL \rightarrow ZnO$$
$$CdL \rightarrow CdO \cdot CdCO_3 \rightarrow CdO$$

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