

SPECTRAL AND THERMAL STUDIES OF Mn(II), Co(II), Ni(II), Cu(II), Zn(II) AND Cd(II) COMPLEXES WITH 3-METHYLGLUTARIC ACID

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Abstract

Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 3-methylglutarates were prepared as solids with general formula $MC_6H_8O_4 \cdot nH_2O$, where $n=0-8$. Their solubilities in water at 293 K were determined ($7.0 \cdot 10^{-2} - 4.2 \cdot 10^{-3} \text{ mol dm}^{-3}$). The IR spectra were recorded and thermal decomposition in air was investigated. The IR spectra suggest that the carboxylate groups are mono- or bidentate. During heating the hydrated complexes lose some water molecules in one (Mn, Co, Ni, Cu) or two steps (Cd) and then mono- (Cu) or dihydrates (Mn, Co, Ni) decompose to oxides directly (Mn, Cu, Co) or with intermediate formation of free metals (Co, Ni). Anhydrous Zn(II) complex decomposes directly to the oxide ZnO.

Keywords: complexes, IR spectra, 3-methylglutaric acid, thermal analysis

Introduction

3-Methylglutaric acid $C_4H_8(COOH)_2$ is a crystalline solid soluble in hot water, ethanol and ether, and sparingly soluble in benzene and chloroform [1]. The complexes of Ag(I) and Pb(II) were prepared as solids sparingly soluble in water and those of Na(I), $NH_4(I)$ and Ca(II) as soluble in water. The rare earth element 3-methylglutarates were prepared as solids with general formula $Ln_2(C_6H_8O_4)_3 \cdot nH_2O$, soluble in water [2]. Their solubilities are of the order $10^{-2} \text{ mol dm}^{-3}$ and change periodically in the lanthanide series. During heating the hydrated complexes are dehydrated in one step and next the anhydrous ones decompose directly to oxides Ln_2O_3 , CeO_2 , Pr_6O_{11} and Tb_4O_7 . (Ce, Pr, Tb–Lu) or with intermediate formation $Ln_2O_2CO_3$ (Y, La, Nd–Gd). In the studied complexes the carboxylate groups are bidentate and the complexes are polymers.

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-methylglutaric acid in solid state and to study their properties and thermal decomposition in air.

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

Complex	Metal content/%		C/%		H/%		Solubility·10 ⁻² / mol dm ⁻³
	calc.	found	calc.	found	calc.	found	
Mn[C ₄ H ₈ (COO) ₂]·5H ₂ O	19.01	19.03	24.91	25.02	6.23	6.02	4.58
Co[C ₄ H ₈ (COO) ₂]·3H ₂ O	22.93	23.10	28.02	28.70	5.45	5.57	3.50
Ni[C ₄ H ₈ (COO) ₂]·3H ₂ O	22.87	23.00	28.03	28.75	5.45	5.50	1.91
Cu[C ₄ H ₈ (COO) ₂]·2H ₂ O	26.09	26.10	29.57	30.05	4.92	5.02	0.42
Zn[C ₄ H ₈ (COO) ₂]	31.22	31.25	34.38	34.23	3.82	3.82	7.00
Cd[C ₄ H ₈ (COO) ₂]·8H ₂ O	28.07	28.07	17.98	18.20	5.99	5.83	4.19

Experimental

The complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 3-methylglutaric acid were prepared by dissolving M(II) ion carboxylates in a hot solution of 0.1 M solution of 3-methylglutaric acid and after filtration of an excess of carbonate their crystallization at room temperature. The precipitates formed were filtered off, washed with water and dried at 303 K to a constant mass. The content of metal ions in the complexes was determined by AAS method on an atomic absorption spectrophotometer AAS-3 (Carl-Zeiss, Jena). The carbon and hydrogen content were determined by elemental analysis on a Perkin Elmer CHN 2400 analyzer. The number of crystallization water molecules was determined from TG curves and by isothermal heating of the hydrated complexes. The experimental results confirm the calculated data (Table 1). The IR spectra of the complexes and spectra of 3-methylglutaric acid and its sodium salt were recorded as KBr discs on a Specord M-80 spectrophotometer (4000–400 cm^{-1}). The solubilities of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes were determined by measuring the concentration of Mn(II) ions in saturated (under isothermal conditions) solution using AAS method. Thermal stabilities of the prepared complexes were investigated by TG, DTG and DTA curves. Measurements were made with Q-1500 derivatograph with Derill converter at a heating rate of 10 K min^{-1} with full scale. The samples of 100 mg were heated in platinum crucibles in static air to 1273 K with a sensitivity TG=100 mg. The DTG and DTA sensitivities are regulated by computer Derill program. The products of decomposition were calculated from TG curve and were verified by diffractogram registration.

Results and discussion

3-Methylglutarates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared as fine crystalline solids with colour characteristic of M(II) hydrated ions, with a molar ratio of metal to organic ligand of 1.0:1.0. The complexes of Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) were prepared as hydrates with different degree of hydration (Table 1). Only Zn(II) complex was obtained as anhydrous one. The prepared complexes are characterized by diversity of their structure [3]. Very often the complexes of Co(II) and Ni(II) are isostructural, but in this case they are characterized by different structures.

3-Methylglutarates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are soluble in water (Table 1). Their solubilities are of the order $10^{-2} \text{ mol dm}^{-3}$, except for the Cu(II) one, the solubility of which is equal to $4.2 \cdot 10^{-3} \text{ mol dm}^{-3}$. The solubilities of the prepared complexes increase in the order: $\text{Cu} \ll \text{Ni} < \text{Co} < \text{Cd} < \text{Mn} < \text{Zn}$. Usually the complexes of Cu(II) with carboxylic acids are more sparingly soluble in water than those of Mn(II), Co(II), Ni(II), Zn(II) and Co(II) [4, 5].

Infrared spectra

The 3-methylglutaric acid exhibits a strong absorption band at 1696 cm^{-1} of C=O in COOH. When the acid is converted to the salt, the stretching vibration band of C=O at 1696 cm^{-1} disappears, whereas the bands of asymmetric vibrations $\nu_{\text{as}}(\text{OCO})$ at $1550\text{--}1588$ and the bands of symmetric vibrations $\nu_{\text{s}}(\text{OCO})$ at $1404\text{--}1440\text{ cm}^{-1}$ appear. In the IR spectra of the prepared complexes exhibit broad absorption bands with max. at $3400\text{--}3448$, and narrow bands of $\delta(\text{H}_2\text{O})$ at $1600\text{--}1630\text{ cm}^{-1}$, confirming the presence of water molecules linked by hydrogen bonds, and the bands of metal-oxygen bond at $520\text{--}540\text{ cm}^{-1}$.

In the IR spectrum of Zn(II) complex the bands of $\nu(\text{OH})$ and $\delta(\text{H}_2\text{O})$ are absent, which confirms the anhydrous character of this compound. The IR spectra of Mn(II), Co(II), Ni(II) and Cd(II) 3-methylglutarates are similar to each other, which suggests similar mode of metal-organic ligand coordination. The bands $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ for these complexes appear at $1568\text{--}1576$ and $1404\text{--}1416\text{ cm}^{-1}$, respectively and are shifted to lower frequencies compared to those bands of the sodium salt (1580 and 1460 cm^{-1}). In the IR spectrum of Zn(II) complex the bands $\nu_{\text{as}}(\text{OCO})$ appear at 1550 and $\nu_{\text{s}}(\text{OCO})$ at 1440 cm^{-1} and are also shifted to lower frequencies.

In the IR spectrum of Cu(II) complex the bands $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ appear at 1588 and 1408 cm^{-1} , and are shifted to higher and to lower frequencies, respectively compared to those bands in free ion. The values $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$ for Mn(II), Co(II), Ni(II) and Cd(II) are similar to each other ($\Delta\nu = 160\text{ cm}^{-1}$) and are higher than for the sodium salt ($\Delta\nu = 120\text{ cm}^{-1}$), whereas for Zn(II) complex $\Delta\nu (110\text{ cm}^{-1})$ is almost close to that for the sodium salt. The values $\Delta\nu$ for Cu(II) complex has the highest value ($\Delta\nu = 180\text{ cm}^{-1}$).

On the basis of the spectroscopic criteria [6–9], our previous work [10–12] and other authors [13], it is possible to suggest that carboxylate group in the complexes of Mn(II), Ni(II), Co(II), Zn(II) and Cd(II) are bidentate bridging whereas in the Cu(II) one as monodentate. In the complexes with monodentate carboxylate groups $\nu_{\text{as}}(\text{OCO})$ increases and $\nu_{\text{s}}(\text{OCO})$ decreases, whereas in the complexes with bidentate bridging OCO group, the $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ are shifted in the same direction. The oxygen atoms of carboxylate group are not only coordinated to metal ion, but they may be linked by hydrogen bonds to the water of crystallization [9], which influences, first of all, on the position of $\nu_{\text{as}}(\text{OCO})$, which are more diagnostic values than $\nu_{\text{s}}(\text{OCO})$.

The stretching vibrations of coordinated carboxyl group are determined by combined effect of the mass, radius, negativity of the central atom and some other factors [15] and hence the results must be interpreted with certain probability. The water molecules are probably in inner sphere of the complexes except for Cd(II) complex in which there are inner and outer sphere water molecules, but the coordinated and uncoordinated water molecules are not distinguished by the thermogravimetric curve. The full interpretation of the mode of metal–ligand coordination would be possible after determination of the crystallographic and molecular structure of monocrystals, but they were not obtained so far. The frequencies of the M–O stretching vibrations increases in the order: Ni=Cu=Zn<Mn<Co=Cd. The magnitude of the M–O frequencies and that of the stability constants of the complexes change generally in the same

direction [15]. This is to be expected, since an increase in the M–O bond order means higher stability of the complex. However, in view of the fact that conjugation of the M–O, C–O and C–C bonds may occur in the chelate ring of the complex, and hence there will be no pure M–O stretching vibrations and the results must be interpreted with great caution.

Table 2 Frequencies of maximum of absorption bands in IR spectra of 3-methylglutarates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Na(I) (cm^{-1})

Complex	$\nu(\text{OH})$	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{s}}(\text{OCO})$	$\nu_{\text{as}}-\nu_{\text{s}}$	$\nu(\text{M}-\text{O})$
MnL·5H ₂ O	3400	1568	1404	164	525
CoL·3H ₂ O	3416	1568	1408	160	530
NiL·3H ₂ O	3448	1576	1416	160	520
CuL·2H ₂ O	3400	1588	1408	180	520
ZnL	–	1550	1440	110	520
CdL·8H ₂ O	3425	1570	1410	160	530
Na ₂ L	3450	1580	1460	120	540

Thermal analysis

The 3-methylglutarates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are stable at room temperature. During heating they decompose in two or three steps (Figs 1–3, Table 3). The hydrated complexes of Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) are stable up to 323–373 K and on farther heating they lose some water molecules in one (Mn, Co, Ni, Cu) or two steps (Cd) over the range 323–453 and 323–593 K, respec-

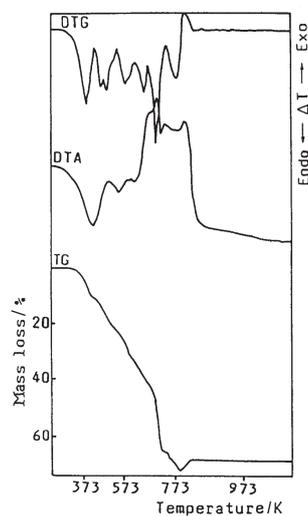


Fig. 1 TG, DTG and DTA curves of $\text{Co}[\text{C}_4\text{H}_8(\text{COO})_2] \cdot 3\text{H}_2\text{O}$

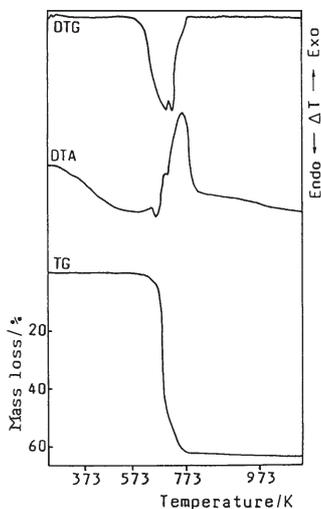


Fig. 2 TG, DTG and DTA curves of $\text{Zn}[\text{C}_4\text{H}_8(\text{COO})_2]$

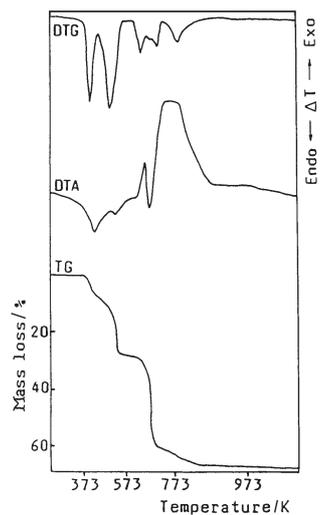


Fig. 3 TG, DTG and DTA curves of $\text{Cd}[\text{C}_4\text{H}_8(\text{COO})_2] \cdot 8\text{H}_2\text{O}$

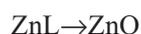
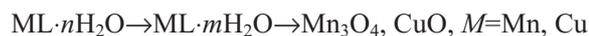
tively. The dehydration process is connected with endothermic effect at 473–533 K (for Cd: at 473 and 553 K). Dihydrated complexes of Mn(II), Co(II), Ni(II) and Cd(II), monohydrated complex of Cu(II) and anhydrous one of Zn(II) are stable up to 415–613 K and then decompose in different ways. The dihydrated 3-methylglutarates of Co(II) and Ni(II) decompose over the range 415–793 K to free metals and next are oxidized to oxides (NiO , Co_3O_4) over the range 793–823 K. The hydrated complexes of Mn(II), Cu(II), Cd(II) and anhydrous complex of Zn(II) decompose directly to oxides over the range 553–853 K. The temperature of oxide formation increases from

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

Complex	$\Delta T_1/\text{K}$	Mass loss/%		Loss of H ₂ O/ mol	$\Delta T_2/\text{K}$	Mass loss/%		$\Delta T_3/\text{K}$	Mass loss/%		T_K/K
		calc.	found			calc.	found		calc.	found	
MnL [*] ·5H ₂ O	323–523	18.68	19.0	3	–	–	–	613–843	73.58	73.5	843
CoL·3H ₂ O	323–413	6.95	7.0	1	415–793	73.50	73.0	793–823	68.99	69.0	793
NiL·3H ₂ O	323–413	7.01	7.0	1	523–793	77.13	77.0	793–823	70.89	71.0	793
CuL·2H ₂ O	373–453	7.40	7.5	1	–	–	–	553–803	67.35	67.5	803
ZnL	–	–	–	–	–	–	–	593–783	61.50	61.2	783
CdL·8H ₂ O	373–453	8.99	9.0	2	–	–	–	–	–	–	–
–	453–593	26.90	27.0	4	–	–	–	613–853	67.93	68.0	853

L^{*} – C₄H₈(COO)₂²⁻, ΔT_1 – temperature range of dehydration, ΔT_2 – temperature range of decomposition to free metals, ΔT_3 – temperature range of decomposition to oxides

783 for ZnO to 853 K for CdO. The temperatures of oxide formation increase in the order: Zn<Co=Ni<Cu<Mn<Cd with decreasing electronegativity of the metal (except for Zn). The results indicate that the thermal decomposition of the prepared complexes can be presented as:



Conclusions

Complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 3-methylglutaric acid were prepared as solids with a molar ratio of metal to organic ligand of 1:1, soluble in water. The carboxylate group in the complexes of Mn(II), Ni(II), Co(II), Zn(II) and Cd(II) are bidentate bridging whereas in the Cu(II) one as monodentate. The oxygen of carboxylate group are not only coordinated to metal ion, but they may be linked by hydrogen bonds to the water of crystallization. The water molecules are probably in inner sphere of the complexes except for the Cd(II) complex in which there are inner and outer sphere water molecules. During heating the hydrated complexes lose some water molecules in one (Mn, Co, Ni, Cu) or two steps (Cd) and then mono- (Cu) or dihydrates (Mn, Co, Ni) decompose to oxides directly (Mn, Cu, Co) or with intermediate formation of free metals (Co, Ni). Anhydrous Zn(II) complexes directly to the oxide ZnO.

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