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NEW COMPLEXES OF SOME *d*-ELECTRON ELEMENTS WITH 3-METHYLADIPIC ACID

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Abstract

Conditions for the preparation of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) 3-methyladipates were investigated and their qualitative composition and magnetic moments were determined. The IR spectra and powder diffraction patterns of the complexes prepared of the general formula $M(C_7H_{10}O_4)\cdot nH_2O$ (n=0–11) were recorded and their thermal decomposition in air were studied. During heating the hydrated complexes are dehydrated in one (Co, Ni) or two steps (Mn, Zn) losing all crystallization water molecules (Co, Ni) or some water molecules (Mn, Zn) and then anhydrous (Co, Ni, Cu) or hydrated complexes (Mn, Zn) decompose directly to oxides (Mn, Co, Zn) or with intermediate formation the mixture of M+MO (Ni, Cu). The carboxylate groups are bidentate (Mn, Co, Ni, Cu) or monodentate (Zn). The complexes exist as polymers. The magnetic moments for the paramagnetic complexes of Mn(II), Co(II), Ni(II) and Cu(II) attain values 5.48, 4.49, 2.84 and 1.45 B.M., respectively.

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

Introduction

3-Methyladipic acid $C_5H_{10}(COOH)_2$ is a crystalline solid soluble in water, ether, acetone, chloroform and acetic acid, sparingly soluble in benzene, toluene and xylene, and practically insoluble in petroleum benzine [1]. The salts of Na(I) and K(I) [1, 2] are soluble in water, whereas the complexes of Cu(II), Ag(I) and Ba(II) [1] are sparingly soluble in water. Ikeda *et al*. [3] determined the stability constants of rare earth element 3-methyladipates by potentiometric method. The stability constants of 3-methyladipates are smaller than those of adipates. The 3-methyladipates of rare earth elements (Y, La–Lu) [4] have been prepared as hydrates with general formula $Ln_2L_3\cdot nH_2O$, sparingly soluble in water. The IR spectra of the prepared complexes suggest that the carboxylate groups are bidentate chelating. During heating the complexes lose all crystallization water molecules in one (Ce–Lu) or two steps (Y) (exception of La complex which undergoes to monohydrate) and then decompose directly to oxides (Y, Ce) or with intermediate formation of oxocarbonates $Ln_2O_2CO_3$ (Pr–Tb) or $Ln_2O(CO_3)_2$ (Gd–Lu).

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Only La(III) complex decomposes in four steps forming additionally unstable $La_2(C_7H_{10}O_4)CO_3$.

The aim of our work was to prepare the complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 3-methyladipic acid in solid state under the same conditions and to study their properties and thermal decomposition in air.

Experimental

The complexes of Mn(II), Co(II), Ni(II) and Zn(II) with 3-methyladipic acid were prepared by dissolving the fresh precipitated metal(II) carbonates in hot 0.2 M solution of 3-methyladipic acid, filtering excess of carbonate and crystallizing at room temperature. The precipitation formed were filtered off and washed with hot water. The complex of Cu(II) with 3-methyladipic acid was prepared by adding 0.2 M solution of ammonium 3-methyladipate (pH 5.0) to a hot 0.3 M solution of copper(II) nitrate. The precipitate formed was heated in mother solution for 0.5 h, filtered off and washed with hot water to remove ammonium ions. All precipitates were 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 content of metal was determined by AAS method using 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 define temperature. The experimental results of the analysis confirm the calculated data (Table 1). The IR spectra of the prepared 3-methyladipates and spectra of 3-methyladipic acid and its sodium salt were recorded as KBr discs on a Specord M–80 spectrophotometer (4000–400 cm^{-1}). The powder diffraction patterns of the prepared complexes and the products of their decomposition were recorded by using X-ray 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 $Co[Hg(SCN)_4]$. 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 [5]. The samples were heating in air to 1273 K.

Table 1 Analytical data and colour of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) 3-methyladipates

Complex	*M*%		C%		H%		Colour	*M*
	calc.	found	calc.	found	calc.	found		
$MnL\cdot 4H_2O$	19.29	19.3	29.47	30.0	6.31	6.3	beige	284.0
$CoL\cdot 2H_2O$	23.32	23.4	33.20	33.2	5.53	5.5	violet	253.0
$NiL\cdot 2H_2O$	23.32	23.5	33.24	33.3	5.54	5.5	green	252.7
CuL	28.67	28.7	37.92	34.0	4.51	4.4	blue	221.5
$ZnL\cdot 11H_2O$	15.52	15.3	19.93	20.0	7.59	7.7	white	421.4

$L – C_7H_{10}O_4^{2-}$

Results and discussion

3-Methyladipates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared as solids of general formula $M(C_7H_{10}O_4)\cdot nH_2O$, where n=4 for Mn, n=2 for Co and Ni, n=0 for Cu and n=11 for Zn having colour characteristic for hydrated metal(II) ions. The complexes of Ni(II), Cu(II) and Zn(II) are crystalline, whereas those of Mn(II) and Zn(II) are radiographically amorphous and form glass. All complexes with exception of Cu(II) complex are well soluble in water.

The susceptibilities of paramagnetic Mn(II), Co(II), Ni(II) and Cu(II) complexes calculated from results of magnetic measurements at 295 K were corrected by measuring the diamagnetic susceptibility of ligand. The magnetic moments were calculated by using formula $\mu_{eff}=2.84(\chi_M T)^{1/2}$. The complex of Zn(II) was diamagnetic. The magnetic moments determined for the complexes of Mn(II), Co(II), Ni(II) and Cu(II) are equal to: 5.48, 4.49, 2.84 and 1.46 B.M., respectively (Table 1). The magnetic moments determined for Mn(II) and Ni(II) complexes are similar to theoretical values for octahedral complexes with configuration d^5 and d^8, respectively. The value of μ_{eff} for Mn(II) complex shows on high spin – only configuration (μ_{eff}=5.6–6.10 B.M.) [6] and octahedral structure. For Co(II) complex the measured magnetic moment (4.49 B.M.) differs to some extent from spin – only moment. Its magnetic moment, instead of spin – only moment 3.88 B.M. characteristic for d^7 configuration (three unpaired electrons) is equal to 4.49 B.M. Literature data [6, 7] show that measured magnetic moments for Co(II) complexes with different ligand attain values 4.3–5.28 B.M. The magnetic moment value (1.45 B.M.) for Cu(II) complex is smaller than theoretical value 1.72 B.M. for the tetrahedral complex with configuration d^9 and polymeric structure. The small value of magnetic moment confirms the polymeric structure of the complex, because in polymeric compounds Cu–Cu action reduces its value.

All prepared 3-methyladipates 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 at 1700 cm^{-1} disappear, whereas the band of asymmetric vibrations $\nu_{as}(OCO)$ at 1564–1588 cm^{-1} and the bands of symmetric vibrations $\nu_s(OCO)$ at 1384–1420 cm^{-1} appear. In the IR spectra of Mn(II), Co(II), Ni(II), and Zn(II) 3-methyladipates broad absorption bands of ν(OH) with max. at 3424–3432 cm^{-1} and narrow bands of $\delta(H_2O)$ at 1620–1630 cm^{-1} are observed confirming the presence of crystallization water molecules linked by hydrogen bonds. Those bands do not appear in the IR spectrum of Cu(II) complex confirming its anhydrous character. In the spectra of all prepared complexes similarly as in the IR spectrum of free acid there are the bands of CH_3 vibrations at 2960, 2930 and 1164–1172 cm^{-1}, and the bands of C–H vibrations at 1330–1350, 1100, 900–700 cm^{-1}. The splitting of the absorption bands of valency vibrations $\nu_{as}(OCO)$ and $\nu_s(OCO)$ ($\Delta\nu=\nu_{as}-\nu_s$) in the IR spectra of Mn(II) and Cu(II) have values 152 and 168 cm^{-1} and those of Co(II), Ni(II) and Zn(II) are bigger and amount to 180–188 cm^{-1}. The values of Δν for all complexes (except of Mn(II) one) are bigger than for the sodium salt (Δν=160 cm^{-1}) suggesting the great degree of ionic bond character in these complexes. The bands of $\nu_{as}(OCO)$ in the IR spectra of Mn(II), Co(II), Ni(II) and Zn(II) do not change practically their position and the bands $\nu_s(OCO)$ are shifted to lower frequencies or do not change their position compared to those for the sodium salt. In the IR spectrum of Cu(II) 3-methyladipate the band ν_{as}(OCO) is shifted to higher and the band of ν_s(OCO) to lower frequencies compared to those bands for the sodium salt. On the basis of spectroscopic criteria [7–9], $\Delta\nu$ values and shifts of the ν_{as}(OCO) and ν_s(OCO) compared to the bands for the sodium salt and our previous works [4, 5] it is possible to suggest that in the complexes of Mn(II), Co(II), Ni(II) and Cu(II) the carboxylate groups act as bidentate and in the Zn(II) complex as monodentate. In the Zn(II) and Mn(II) complexes there are probably both inner and outer sphere water molecules, whereas in the complexes of Co(II) and Ni(II) water is only in inner sphere. Taking into account spacial structure of the 3-methyladipate ligand and the complexes it is possible to suggest, that the prepared 3-methyladipates exist as polymers.

Table 2 Frequencies of characteristic absorption bands in IR spectra of Na(I), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) 3-methyladipates [cm^{-1}] and the magnetic moments

Complex	ν(OH)	δ(H_2O)	ν_{as}(OCO)	ν_s(OCO)	ν_{as}–ν_s	μ_{eff}/B.M.
$MnL\cdot 4H_2O$	3432	1630	1564	1408	156	5.48
$CoL\cdot 2H_2O$	3432	1620	1568	1384	184	4.49
$NiL\cdot 2H_2O$	3432	1620	1568	1384	184	2.84
CuL	–	–	1588	1420	168	1.45
$ZnL\cdot 11H_2O$	3432	1630	1572	1384	188	–
$Na_2L\cdot nH_2O$	3432	–	1568	1408	160	–

L – $C_7H_{10}O_4^{2-}$

The complexes prepared are stable at room temperature. During heating in air they decompose in different ways (Table 3). Hydrated complexes of Mn(II), Co(II), Ni(II) and Zn(II) are stable up to 323 K. Dihydrated complexes of Co(II) and Ni(II) lose in one step all crystallization water molecules over the range 323–583 K forming anhydrous compounds. The hydrated complexes of Mn(II) and Zn(II) heated lose some crystallization water molecules in two steps over the range 323–613 K forming partially hydrated complexes, which are dehydrated and decompose simultaneously. The dehydration process is connected with strong endothermic effect. The anhydrous complexes of Co(II), Ni(II) and Cu(II) during heating decompose in two or three steps over the range 373–673 to 613–883 K. 3-Methyladipate of Co(II) decomposes directly to Co_3O_4, whereas the complexes of Ni(II) and Cu(II) decompose to MO with intermediate formation of mixture of M+MO. Dihydrated Mn(II) complex and pentahydrated Zn(II) complex heated decompose directly to Mn_3O_4 and ZnO, respectively. The dehydration processes are connected with endothermic effect, whereas the combustion of organic ligand, products of decomposition and oxidation of free metal to oxide proceed with strong exothermic effects. The temperature of oxide formation change in the order: Cu<Co<Mn<Zn<Ni from 613 for Cu(II) to 883 for Ni(II).

The results indicate, that the prepared 3-methyladipates decompose in the following way:

Table 3 Thermoanalytical data of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) 3-methyladipates

Complex	ΔT_1/K	Mass loss/%		nH$_2$O/ mol	ΔT_2/K	Mass loss%		nH$_2$O/ mol
		found	calc.			found	calc.	
MnL·4H$_2$O	323–523	6.31	6.0	1	533–573	12.64	12.5	1
CoL·2H$_2$O	323–563	14.24	14.5	2	–	–	–	–
NiL·2H$_2$O	323–583	14.62	14.5	2	–	–	–	–
CuL	–	–	–	–	–	–	–	–
ZnL·11 H$_2$O	323–583	8.54	8.0	2	573–673	25.65	25.0	4

Table 3 Continued

Complex	ΔT_3/K	Mass loss/%		ΔT_4/K	Mass loss/%		T_K/K
		found	calc.		found	calc.	
MnL·4H$_2$O	–	–	–	573–723	73.25	73	723*
CoL·2H$_2$O	–	–	–	573–703	68.28	68	703**
NiL·2H$_2$O	583–823	73.64	73	823–883	70.45	70	883
CuL	373–613	67.71	66	613–693	64.09	64	613
ZnL·11 H$_2$O	–	–	–	613–713	80.69	81	713

L – $C_7H_{10}O_4^{2-}$
ΔT_1, ΔT_2 – temperature range of dehydration
ΔT_3 – temperature range of decomposition to M+MO
ΔT_4 – temperature range of decomposition to MO, *Mn_3O_4, **Co_3O_4
T_K – temperature over which oxides exist

$$MnL{\cdot}4H_2O \rightarrow MnL{\cdot}3H_2O \rightarrow MnL{\cdot}2H_2O \rightarrow Mn_3O_4,$$

$$CoL{\cdot}2H_2O \rightarrow CoL \rightarrow Co_3O_4,$$

$$NiL{\cdot}2H_2O \rightarrow NiL \rightarrow Ni{+}NiO \rightarrow NiO,$$

$$CuL \rightarrow Cu{+}CuO \rightarrow CuO,$$

$$ZnL{\cdot}11H_2O \rightarrow ZnL{\cdot}9H_2O \rightarrow ZnL{\cdot}5H_2O \rightarrow ZnO.$$

Conclusions

3-Methyladipates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared as solids with molar ratio of metal to organic ligand of 1.0:1.0. The complexes of Mn(II), Co(II), Ni(II) and Zn(II) were prepared as hydrates, whereas the complex of Cu(II) as anhydrous one. When heated the hydrated complexes were dehydrated in one (Co, Ni) or two steps (Mn, Zn) losing all crystallization water molecules (Co, Ni) or some water molecules (Mn, Zn) and then the anhydrous (Co, Ni, Cu) or partially hydrated complexes (Mn, Zn) decompose directly to oxides (Mn, Co, Zn) or with intermediate formation the mixture of M+MO (Ni, Cu). The complexes exist probably as polymers. The magnetic moments for paramagnetic complexes of Mn(II), Co(II), Ni(II) and Cu(II) attain values 5.48, 4.49, 2.84 and 1.45 B.M., respectively.

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