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Thermal, Spectral and Magnetic Studies of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Mesaconic Acid

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Conditions for the preparation of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) mesaconates were investigated and their quantitative composition and magnetic moments were determined. The IR spectra and powder diffractograms of the complexes prepared with general formula $M(C_5H_4O_4)\cdot nH_2O$ (where n = 3 for Mn, Co, n = 2 for Ni, Cu and n = 0 for Zn) were recorded and their thermal decomposition in air was studied. During heating, the hydrated complexes are dehydrated in one (Ni, Co, Cu) or two (Mn) steps and next the anhydrous complexes of Mn(II) and Zn(II) decompose directly to oxides. The complex of Co(II) decomposes to oxide with intermediate formation of the free metal, whereas those of Ni(II) and Cu(II) complexes decompose to oxides with intermediate formation of mixture of free metal and its oxide. The effective magnetic moments for the paramagnetic complexes of Mn(II), Co(II), Ni(II) and Cu(II) attain values 5.32, 4.77, 3.12 and 1.73 B.M., respectively.

Key words: DTA, IR spectra, magnetic moments, mesaconates, synthesis, TG

Mesaconic acid $C_3H_4(COOH)_2$ is a crystalline solid soluble in water, ethanol, ether, $CHCl_3$ and CS_2 [1]. Its complexes of metal ions are little known. Mesaconates of NH_4^+, Na, K, Ca and Ba [1] were prepared as solids soluble in water, whereas the complexes of Ag(I), Hg(II), Cu(II) and Pb(II) as sparingly soluble in water. The complex of Cu(II) was prepared as dihydrate, that of Hg(II) as monohydrate and those of Ag(I) and Pb(II) as anhydrous ones. The complexes prepared have not been studied in detail. The complexes of Y(III) and lanthanides(III) with mesaconic acid [2] were prepared as hydrates with molar ratio of metal to organic ligand of 2:3, sparingly soluble in water. During heating, the hydrate complexes are dehydrated in one (Y, Nd – Lu) or two steps (La – Pr) and then decompose directly to oxides (Y, Ce, Pr, Sm, Gd – Lu) or with intermediate formation $Ln_2O_2CO_3$ (La, Nd, Eu). The IR spectra of the prepared mesaconates suggest that carboxylate groups are bidentate bridging and chelating.

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

EXPERIMENTAL

The complexes of Mn(II), Co(II), Ni(II) and Zn(II) with mesaconic acid were prepared by dissolving the fresh precipitated metal(II) carbonates in hot 0.2 M solution of mesaconic acid, filtering the excess of carbonate and crystallization at room temperature. The precipitates formed were filtered off, washed with hot water. The complex of Cu(II) with mesonic acid was prepared by adding the equivalent amount of 0.2 M solution of ammonium mesaconate (pH 5) to a hot 0.2 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 NH_4^+ ions. All precipitates prepared 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 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 isothermal heating of the hydrated complexes at define temperature. The experimental results of these analyses confirm the calculated data. The IR spectra of the prepared complexes and spectra of mesaconic 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 mesaconates and the products of their decomposition were recorded using X-ray diffractometer HZG 4 AZ. The magnetic susceptibility of the prepared complexes was measured on a magnetic balance (Scherwood Scientific MSB MK I) using as a standard $Co[Hg(SCN)_4]$. The thermal stability of the prepared mesaconates was investigated by method described earlier [3]. The products of decomposition were calculated from TG curves and verified by recording X-ray diffractograms and IR spectra.

RESULTS AND DISCUSSION

Mesaconates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared as solids with colours characteristic for hydrated metal(II) ions with the molar ratio of metal to organic ligand of 1.0 : 1.0 and with general formula $M(C_5H_4O_4)\cdot nH_2O$, where n = 3 for Mn, Co, n = 2 for Ni, Cu and n = 0 for Zn. The complexes prepared are crystalline solids characterized by different structure. All the complexes, except of Cu(II) complex, are very well soluble in water.

The susceptibility values for 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) is diamagnetic. The magnetic moments determined for the complexes of Mn(II), Ni(II), Co(II) and Cu(II) are equal to: 5.32, 4.77, 3.12 and 1.73 B.M., respectively. The magnetic moments determined for the complexes of Ni(II) and Mn(II) 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} = 5.6–6.10 B.M. [4]) and octahedral structure. For Co(II) complex the measured magnetic moment (4.75 B.M.) differs to some extent from the 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 4.75 B.M.. Literature data [4,5] show that measured magnetic moments for Co(II) complexes with different ligands attain values 4.3–5.2 B.M.. The magnetic moment value (1.73 B.M.) for Cu(II) complex is similar to the theoretical spin-only value (1.7–2.2 B.M.) [4,5].

All prepared complexes exhibit similar solid state IR spectra (Table 1). When the acid is converted to the complex, the band of stretching vibrations of C=O group, ν(C=O) in COOH at 1680 cm^{-1} disappears, whereas the bands of asymmetrical vibrations ν_{as}(OCO) at 1592–1536 cm^{-1} and the bands of symmetrical vibrations ν_s(OCO) at 1392–1364 cm^{-1} appear. In the IR spectra of Mn(II), Co(II), Ni(II) and Cu(II) mesaconates there are broad absorption bands ν(OH) with maxima at 3448–3312 cm^{-1} and narrow bands of δ(H_2O) at 1648–1630 cm^{-1} confirming the presence of crystallization water molecules linked by hydrogen bond and the bands of C–H vibrations at 1100, 900–700 cm^{-1}. In the IR spectra of anhydrous Zn(II) mesaconate the bands characteristic for crystallization water molecules are lacking. The splitting for absorption bands of valency vibrations ν_{as}(OCO) – ν_s(OCO) (Δν = $\nu_{as} - \nu_s$) have values 144–176 cm^{-1} and are smaller than for the sodium salt (Δν = 180 cm^{-1}). Only for the Cu(II) complex Δν is greater than for the sodium salt (228 cm^{-1}). In the IR spectra of Mn(II), Co(II) and Ni(II) complexes the bands ν_{as}(OCO) and ν_s(OCO) are shifted to lower frequencies compared to those bands for the sodium salt. In the IR spectra of Cu(II) mesaconate the band ν_{as}(OCO) is shifted to higher and the band of ν_s(OCO) to lower frequencies, whereas for Zn(II) complex the band ν_{as}(OCO) is shifted to lower and the band of ν_s(OCO) to higher frequencies, compared to those bands for the sodium salt. On the basis of spectroscopic criteria [6–8], Δν values and shifts of the ν_{as}(OCO) and ν_s(OCO) compared to the bands for the sodium salt and our previous works [3,9,10], it is possible to suggest that in the complexes of Mn(II), Co(II) and Ni(II) the carboxylate groups act as bidentate bridging, in the complex of Cu(II) – as monodentate and in the Zn(II) complex as bidentate chelating ligands. Zn(II) ions have probably coordination number equal to 4, whereas Co(II), Ni(II) and Mn(II) have C.N. = 6, what is confirmed by magnetic measurements. In the Mn(II) and Co(II) complexes there are probably inner and outer sphere water molecules, whereas in Ni(II) and Cu(II) complexes water is only in the inner sphere.

Table 1. Frequencies of characteristic bands in IR spectra of Na(I), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) mesaconates (cm^{-1}).

Complex	ν(OH)	δ(H_2O)	ν_{as}(OCO)	Δν_{as}(OCO)	ν_s(OCO)	Δν_s(OCO)	$\nu_{as} - \nu_s$
$MnL\cdot 3H_2O$	3448	1648	1552	–16	1376	–12	176
$CoL\cdot 3H_2O$	3424	1640	1548	–20	1384	–4	164
$NiL\cdot 2H_2O$	3248	1630	1556	–8	1384	–8	172
$CuL\cdot 2H_2O$	3312	1640	1592	+24	1364	–14	228
ZnL	–	–	1536	–30	1392	+4	144
$Na_2L\cdot NH_2O$	3424	–	1568	–	1388		180

The complexes prepared are stable at room temparature. During heating in air, they decompose in different ways. Hydrated complexes of Mn(II), Co(II), Ni(II) and Cu(II) are stable up to 333–408 K, whereas anhydrous Zn(II) complex up to 642 K. The thermal stability of the complexes prepared increases in the order:
Ni < Co = Mn < Cu < Zn.

The anhydrous complex of Zn(II) decomposes to ZnO in the temperature range 642–900 K. Trihydrated Mn(II) mesaconate loses crystallization water molecules in two steps and next decomposes to Mn_3O_4 in the temperature range 635–953 K. The hydrated complexes of Co(II), Ni(II) and Cu(II) lose crystallization water molecules in one step (373–476 K). Next anhydrous Co(II) complex decomposes to free metal (557–803 K), which oxidizes to oxide (Table 2), whereas the complexes of Ni(II) and Cu(II) decompose to oxides MO with intermediate formation of mixture of M + MO.

Table 2. Thermoanalytical data of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) mesaconates heated in air atmosphere.

Complex	ΔT_1/K	Mass loss %		N	T_{DTA}/K	ΔT_2/K	Mass loss %		ΔT_3/K	Mass loss %		T_{DTG}/K	T_K/K
		Found	Calc.	H_2O (Mol)			Calc.	Found		Calc.	Found		
$MnL\cdot 3H_2O$	373–451	15.18	15.0	2	423				635–953	67.85	69.0^{xx}		
	482–545	22.78	22.0	1	503							663	953
$CoL\cdot 3H_2O$	373–473	22.40	22.7	3	423	557–803	75.75	75.0	803–873	66.70	66.0^{x}		
									1140–1200	68.91	68.8	653	1200
$NiL\cdot 2H_2O$	333–423	17.04	17.0	2	398	573–832	70.02	70.0^{xxx}	832–1073	66.38	66.0	633	1073
$CuL\cdot 2H_2O$	408–476	15.81	15.0	2	463	476–730	68.50	68.0^{xxx}	730–795	65.05	65.0	513	795
ZnL									642–900	57.93	58.0	710	900

ΔT_1 – temperature range of dehydration, ΔT_2 – temperature range of decomposition to metal or ^{xxx}M + MO, ΔT_3 – temperature range of decomposition to MO, $^{x}Co_3O_4$, $^{xx}Mn_3O_4$, T_K – temperature over which the oxides exist.

The dehydration process is connected with endothermic effect, whereas the combustion of organic ligand, products of its decomposition and oxidation of free metal to oxide proceed with strong exothermic effects. The temperatures of oxides formation increase in the order: Cu < Zn < Mn < Ni < Co.

The results suggest the following schemes of the thermal decomposition:

$MnL\cdot 3H_2O \rightarrow MnL\cdot H_2O \rightarrow MnL \rightarrow Mn_3O_4$; $CoL\cdot 3H_2O \rightarrow CoL \rightarrow Co \rightarrow Co_3O_4 \rightarrow CoO$; $M\cdot 2H_2O \rightarrow ML \rightarrow M + MO \rightarrow MO$, M = Ni, Cu; $ZnL \rightarrow ZnO$.

REFERENCES

1. Beilstein F., Handbuch der organischen Chemie, Bd II, 763(308), Springer Verlag, Berlin, 1920.
2. Brzyska W., Tarnawska A. Twardowska A and Wiśniewska E., *J. Thermal Anal. Cal*., in press.
3. Brzyska W. and Ożga W., *J. Thermal Anal. Cal*., **60**, 123 (2000).
4. Kettle S.F.A., Physical Inorganic Chemistry, Oxford University Press, 1996.
5. Burger K., Coordination Chemistry. Experimental Methods, Akademiai Kiado, Budapest, 1973.
6. Nakamoto K., Infrared Spectra of Inorganic and Coordination Compounds, Wiley, NY, 1997.
7. Manhas B.S. and Trikha A.K., *Indian J. Chem*., **59**, 315 (1982).
8. Bellamy J., The Infrared Spectra of Complex Molecules, Chapman and Hall, London 1975.
9. Brzyska W. and Ożga W., *Polish J. Chem*., **75**, 43 (2001).
10. Brzyska W., Wołodkiewicz W., Rzączyńska Z. and Głowiak T., *Monatsh. Chem*., **126**, 225 (1995).