Thermochimica Acta, 237 (1994) 111–118
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01634-F

The properties and thermal decomposition in air of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,3-dioxyacetates

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(Received 2 August 1993; accepted 18 October 1993)

Abstract

The conditions of the formation of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,3-dioxyacetates were studied and their quantitative composition and solubilities in water at 293 K were determined. The IR spectra and X-ray diffractograms were recorded and their thermal decompositions in air were investigated. During heating, the hydrated complexes $MC_{10}H_8O_6 \cdot nH_2O$ lose some crystallization water molecules in one or two steps, then decompose to the oxides directly (Zn and Cu) or with intermediate formation of the free metals (Co, Ni).

INTRODUCTION

Complexes of benzene-1,3-dioxyacetic acid with Co(II), Ni(II), Cu(II) and Zn(II) are unknown. In our previous papers, we have described the complexes of rare earth elements (Y, La–Lu) with benzene-1,3-dioxyacetic acid [1–3], their preparation, properties in the solid state and thermal decomposition in air. This work is a continuation of our study on the physicochemical properties of metal complexes with benzene-1,3-dioxyacetic acid.

The aim of this work was to prepare Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,3-dioxyacetates in the solid state and to examine their properties and thermal decomposition.

EXPERIMENTAL

Complexes of Co(II) and Ni(II) with benzene-1,3-dioxyacetic acid were prepared by dissolving freshly precipitated Co(II) and Ni(II) carbonates, respectively, in a hot solution of 0.1 M benzene-1,3-dioxyacetic acid, fol-

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lowed by crystallization at room temperature from the solution, after removal by filtration of the excess carbonates. Benzene-1,3-dioxyacetates of Cu(II) and Zn(II) were prepared by adding equivalent quantities of ammonium benzene-1,3-dioxyacetate ($pH \approx 5.9$) to a hot 0.1 M solution of the M(II) nitrate ($pH \approx 5$). The quantitative compositions of the prepared complexes were determined by elemental analysis, by ignition of the complexes to oxides, and from the TG curves. The number of water molecules was determined from the TG curves.

The precipitates formed were mixed in the mother liquor for 0.5 h, filtered and washed with water to remove NH_4^+ ions. All precipitates were dried in room air at 303 K to a constant mass.

The IR spectra of the prepared complexes were recorded by using an EPIR 1725X Perkin-Elmer spectrophotometer within the range 4000–400 cm^{-1}. The samples were prepared as KBr disks.

The X-ray diffraction patterns were recorded on a DRON-2 diffractometer in the range $2\theta = 5-80°$ using Cu $K\alpha$ (Ni-filtered) radiation. Measurements were made according to the Debye–Scherrer method.

The solubilities of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,3-dioxyacetates in water were determined at 293 K. The saturated solutions were prepared under isothermal conditions. The concentrations of Co(II), Ni(II), Cu(II) and Zn(II) were determined using polarography. The measurements were made using an OH-102 Radelkis polarograph.

The thermal stabilities of the complexes obtained were studied. The TG, DTG and DTA curves were recorded. Measurements were made with a Q 1500 D derivatograph at a heating rate of 10 K min^{-1} with a full-scale sensitivity of: TG, 100 mg; DTG, 500 μV; DTA, 500 μV. The paper speed was 2.5 mm min^{-1}. The samples (100 mg) were heated in platinum crucibles in air to 1273 K. Al_2O_3 was used as the standard.

RESULTS AND DISCUSSION

Benzene-1,3-dioxyacetates of Co(II), Ni(II), Cu(II) and Zn(II) were prepared as solids that have the colors characteristic of the hydrated M(II) ions, with the exception of the Cu(II) complex which is green. The molar ratios of metal to organic ligand (calculated on the basis of quantitative compositions) was 1.0:1.0 and the general formula was $MC_{10}H_8O_6 \cdot nH_2O$, where $n = 15$ for Ni(II) and Cu(II), $n = 16$ for Co(II), and $n = 6$ for Zn(II). The prepared complexes were crystalline solids of low symmetry with large unit cells. They are characterized by various structures (Fig. 1).

The complexes of Co(II) and Ni(II) are soluble in water (Table 1). Their solubilities are of the order of 10^{-2} mol dm^{-3}.

The complexes of Zn(II) and Cu(II) are sparingly soluble in water. Their solubilities are of the order of 10^{-3} and 10^{-4} mol dm^{-3}, respectively. The solubilities of the prepared complexes decrease in the order $Ni > Co \gg Zn > Cu$.

TABLE 1

Frequencies for characteristic absorption bands in IR spectra in cm^{-1} and solubilities of Co(II), NI(II), Cu(II) and Zn(II) benzene-1,3-dioxyacetates

Complex [a]	$\nu_{as}(OCO^-)$	$\nu_s(OCO^-)$	$\Delta\nu$ [b]	$\sigma(CH_2)$ in $-CH_2COO$ group	C=C for 1,3-substituted	$\nu(OH)$	Solubility in water at 293 K in $mol\,dm^{-3}$
$CoL \cdot 15H_2O$	1620vs	1358s	262	1417vs	1441m	3420s	1.96×10^{-2}
$NiL \cdot 16H_2O$	1597vs	1377s	220	1427vs	1427m	3462s	3.29×10^{-2}
$CuL \cdot 15H_2O$	1614vs	1341s	273	1424vs	1470m	3396s	1.67×10^{-4}
$ZnL \cdot 6H_2O$	1586vs	1330vs	256	1426vs	1456m	3417s	2.83×10^{-3}
$Na_2L \cdot H_2O$	1605vs	1335s	270	1420m	1435vs	3440s	–

[a] L is $C_{10}H_8O_6^{2-}$. [b] $\Delta\nu = \nu_{as}(OCO) - \nu_s(OCO)$.

TABLE 2

Data on dehydration of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,3-dioxyacetates

Complex	Temp. range of dehyd. I in K	Loss of weight in %		Loss of H_2O in mol	Temp. range of dehyd. II in K	Loss of weight in %		Loss of H_2O in mol	Residue of weight in %		Compounds
		Calcd.	Found			Calcd.	Found		Calcd.	Found	
$CoL \cdot 15H_2O$	313–413	4.88	4.8	1.5	423–548	19.57	19.4	4.5	81.43	80.6	$CoL \cdot 9H_2O$
$NiL \cdot 16H_2O$	318–498	22.08	22.0	7	–	–	–	–	77.92	78.0	$NiL \cdot 9H_2O$
$CuL \cdot 15H_2O$	313–518	19.38	19.0	6	–	–	–	–	80.62	81.0	$CuL \cdot 9H_2O$
$ZnL \cdot 6H_2O$	328–495	22.65	22.0	5	–	–	–	–	77.45	78.0	$ZnL \cdot H_2O$

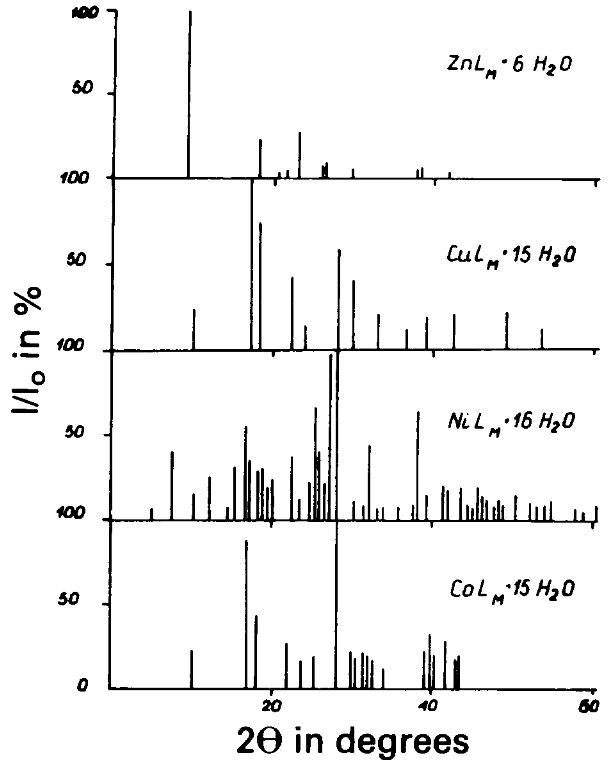

Fig. 1. X-ray diffraction patterns of Co(II), Ni(II) and Zn(II) benzene-1,3-dioxyacetates.

In general, the complexes of Co(II) and Ni(II) with carboxylic acids are soluble in water whereas the complexes of Cu(II) are sparingly soluble: this is determined by the various energies of crystal lattice and metal–ligand bonding.

All the complexes prepared show similar solid-state IR spectra (Table 1) but they differ from the spectrum of the free acid [1]. Their IR spectra show bands of asymmetric vibrations $\nu_{as}(OCO)$ at 1620–1586 cm^{-1}, symmetric vibrations $\nu_s(OCO)$ at 1377–1331 cm^{-1}, and broad absorption bands with maxima at 3396–3462 cm^{-1} confirming the presence of the lattice water. The splittings of the absorption bands of the valency vibrations $\nu_{as}(OCO)$ and $\nu_s(OCO)$ ($\Delta\nu = \nu_{as} - \nu_s$) are very large ($\Delta\nu = 273–220\ cm^{-1}$) and, except for the Ni(II) complex, are similar to that for the sodium salt ($\Delta\nu = 270\ cm^{-1}$). On the basis of the spectroscopic criterion [4–6], the carboxylate group in the complexes studied is bidentate bridging and chelating. The metal–ligand bond has substantial ionic character.

Benzene 1,3-dioxyacetate hydrates of Co(II), Ni(II), Cu(II) and Zn(II) are stable in air and can be stored for several months without change. The complexes decompose in various ways upon heating (Figs. 2–5, Table 2). They are stable up to 313–328 K and then lose some water molecules at

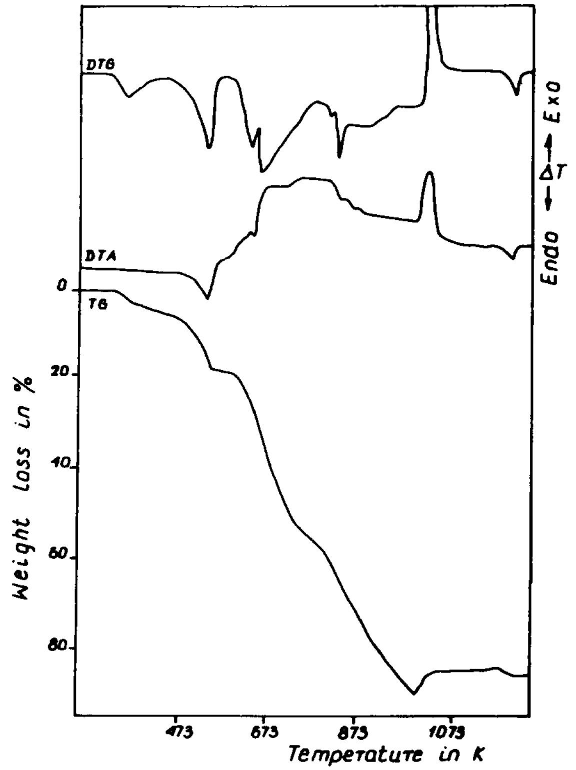

Fig. 2. TG, DTG and DTA curves of $CoC_{10}H_8O_6 \cdot 15H_2O$.

495–548 K in one (Ni(II), Cu(II), Zn(II)) or two (Cu(II)) steps, forming hydrates with fewer water molecules. Table 2 gives the ranges of the dehydration temperatures and quantitative descriptions of the dehydration process for the prepared complexes.

From the results, it appears that the water of crystallization molecules are bonded in three different ways [7]: with an anion (loss at 313–328 K, dehydration I); in the space lattice bonded by a hydrogen bond with an anion or an inner sphere water, as in the Co(II) complex (lost at 423 K, dehydration II); and as coordinated water which is strongly bonded to the metal ion (lost simultaneously with decomposition of organic ligand). Comparing the final temperatures of the first and second steps of the dehydration, it is possible to suggest that the water of crystallization molecules are more strongly bonded with the anion in the Co(II) and Cu(II) complexes than in the Ni(II) and Zn(II) complexes. The complexes do not form anhydrous compounds on heating.

The partially dehydrated complexes, when heated above 495–548 K (Table 3), lost their last water molecules simultaneously with decomposition of the organic ligand. On the DTG curves, there are three peaks for the Co(II) and Cu(II) complexes, and one peak for the Ni(II) and Zn(II)

TABLE 3

Data for decomposition of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,3-dioxyacetates

Complex	Temp. of decomp. peaks (DTG) in K	Temp. of metal formation (DTG) in K	Loss of weight in %		Temp. of oxide formation in K	Residue of weight in %	
			Calcd.	Found		Calcd.	Found
CoL · $9H_2O$	613; 638; 798	993	89.35	89.6	1051 [a] 1188 [b]	14.99 [a] 13.51 [b]	15.2 [a] 14.7 [b]
NiL · $9H_2O$	675	979	89.72	90.0	1018	13.08	13.0
CuL · $9H_2O$	523; 535; 641	–	–	–	878	14.26	14.3
ZnL · H_2O	668	–	–	–	825	20.47	20.3

[a] Co_3O_4. [b] CoO.

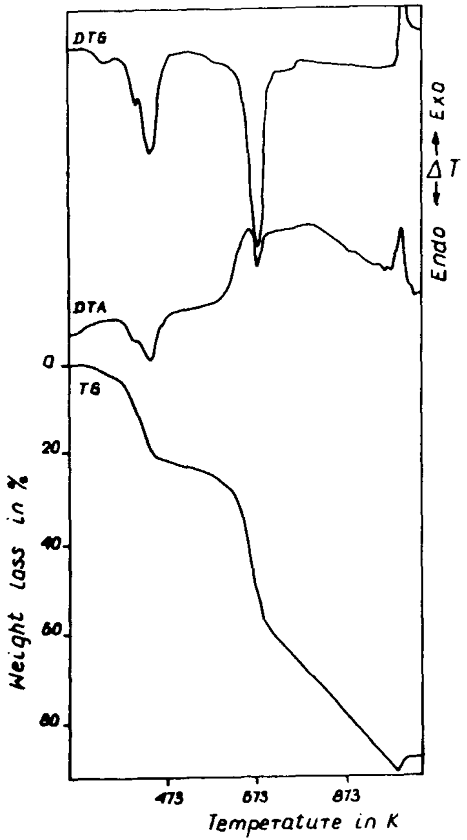

Fig. 3. TG, DTG and DTA curves of $NiC_{10}H_8O_6 \cdot 16H_2O$.

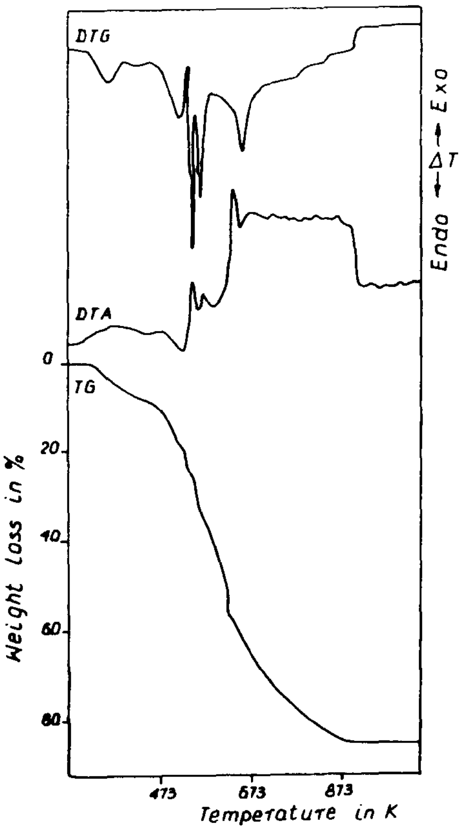

Fig. 4. TG, DTG and DTA curves of $CuC_{10}H_8O_6 \cdot 15H_2O$.

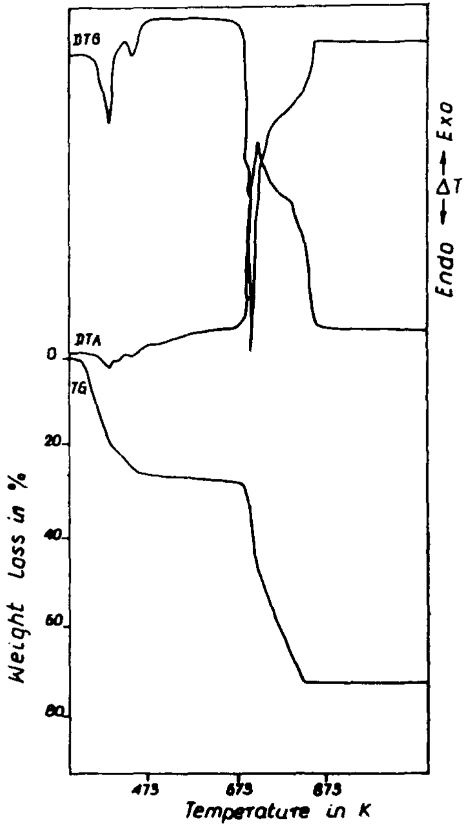

Fig. 5. TG, DTG and DTA curves of $ZnC_{10}H_8O_6 \cdot 6H_2O$.

complexes. This process is accompanied by a strong exothermic effect, which is observed on the DTA curves and is connected with ignition of the decomposition products, carbon and oxidation of the metal (Co, Ni) to oxide. The intermediate products of decomposition were not identified. During heating, the complexes of Co(II) and Ni(II) decompose to the oxides (Co_3O_4, CoO, NiO) with the intermediate formation of free metals at 993 and 973 K, respectively, whereas those of Cu(II) and Zn(II) decompose directly to the oxides (ZnO, CuO). This is confirmed by the high-temperature weight gains evident in the TG curves for the Co and Ni complexes.

The oxides ZnO, CuO, NiO, Co_3O_4 and CoO are formed at 825, 878, 1018, 1051 and 1188 K, respectively. The temperature of oxide formation increases in the order ZnO < CuO < NiO < CoO, with decreasing atomic number of the metal.

The final products of decomposition (CoO, NiO, CuO, ZnO) were identified by X-ray diffraction.

The results indicate that the thermal decomposition of hydrated Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,3-dihydroxyacetates can be presented in the following manner

$$\mathrm{CoL \cdot 15H_2O \rightarrow CoL \cdot 13.5H_2O \rightarrow CoL \cdot 9H_2O \rightarrow Co \rightarrow Co_3O_4 \rightarrow CoO}$$

$$\mathrm{NiL \cdot 16H_2O \rightarrow NiL \cdot 11H_2O \rightarrow Ni \rightarrow NiO}$$

$$\mathrm{CuL \cdot 15H_2O \rightarrow CuL \cdot 12H_2O \rightarrow CuO}$$

$$\mathrm{ZnL \cdot 6H_2O \rightarrow ZnL \cdot H_2O \rightarrow ZnO}$$

where L is $C_{10}H_8O_6^{2-}$.

Summarizing, it is possible to suggest that when the hydrated benzene-1,3-dioxyacetates of Co(II), Ni(II), Cu(II) and Zn(II) are heated in air, they dehydrate in one or two steps, losing some water molecules, and then decompose to form the oxides, either directly (Cu, Zn) or with intermediate formation of the free metals (Co, Ni).

Comparing the temperatures of the decomposition peaks obtained from the TG curves, it was found that the thermal stability of the studied complexes increases with increasing atomic number Z of the metal in the groups Co and Ni, and Cu and Zn.

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