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Properties and thermal decomposition in air atmosphere of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,2-dioxyacetates

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Abstract

The conditions of formation of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,2-dioxyacetates were studied and their quantitative compositions and solubilities in water at 295 K were determined. The IR spectra and X-ray diffractograms for the prepared complexes 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, either directly (Zn) or with intermediate formation of the free metals (Co, Ni and probably Cu).

INTRODUCTION

Benzene-1,2-dioxyacetic acid ($H_2C_{10}H_8O_6$, H_2L) is a multidentate chelating reagent analogous to EDTA. However, stability constants for metal complexes with benzene-1,2-dioxyacetic acid are substantially smaller than those for the corresponding EDTA complexes [1]. The complexes of Zn(II) and Co(II) with benzene-1,2-dioxyacetic acid with the formula $ML \cdot 6.5H_2O$ and that of Ni(II) with the formula $Ni(HL)_2 \cdot 5H_2O$ were prepared as monocrystals, and their structures were determined by X-ray diffraction [2].

As a continuation of our work on the properties and thermal decomposition of rare earth complexes with benzene-1,2-dioxyacetic acid [3–5], we now report the properties and thermal decomposition of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,2-dioxyacetate hydrates during heating in air.

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EXPERIMENTAL

Complexes of benzene-1,2-dioxyacetic acid with Co(II) and Ni(II) were prepared by the addition of a hot 0.1 M solution of acid to a suspension of freshly precipitated metal(II) carbonates; after filtration of excess carbonates, the complexes were crystallized from solution. Cu(II) and Zn(II) benzene-1,2-dioxyacetates were prepared by adding equivalent quantities of ammonium benzene-1,2-dioxyacetate ($pH \approx 5.9$) to a hot 0.1 M solution of the M(II) nitrate ($pH \approx 5$). The precipitates formed were filtered off, and washed with water to remove the NH_4^+ ions. The precipitates were dried at 303 K to a constant mass.

The quantitative compositions of the prepared complexes were determined by elemental analysis, by ignition of the complexes to the oxides and from the TG curves. The number of crystallization water molecules were determined from the TG curve.

The IR spectra for the complexes, and the spectra of benzene-1,2-dioxyacetic acid and its solution salt were recorded as KBr discs on a UR-2 spectrophotometer (range 4000–400 cm^{-1}). The X-ray diffraction patterns of the prepared complexes were measured on a DRON-2 diffractometer using Ni-filtered Cu K radiation. The measurements were made within the range $2\theta = 5–60°$ by means of the Debye–Scherrer method. The solubilities of the Co(II), Ni(II), Cu(II) and Zn(II) complexes in water at 295 K were determined by measuring the concentration of M(II) ions in saturated solution using the polarographic method.

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

RESULTS AND DISCUSSION

Benzene-1,2-dioxyacetates of Co(II), Ni(II), Cu(II) and Zn(II) were obtained as solids, having colours characteristic for the M(II) ions, with a molar ratio of metal to ligand of 1:1 and general formula $MC_{10}H_8O_6 \cdot nH_2O$, where $n = 15$ for Co(II), $n = 30$ for Ni(II) and $n = 8$ for Cu(II) and Zn(II). The prepared complexes are crystalline solids with low symmetry and large unit cells; they are characterized by the diversity of their structures (Fig. 1).

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

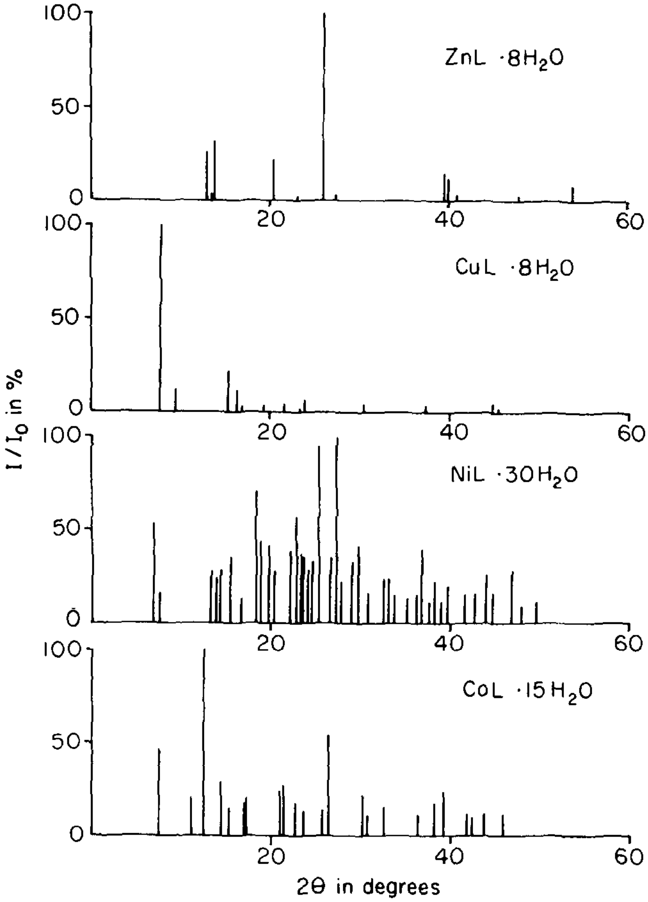

Fig. 1. XRD results for Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,2-dioxyacetates.

10^{-4} and 10^{-5} mol dm^{-3}, respectively. Thus, the solubilities of the prepared complexes decrease in the order Ni ≈ Co ≫ Zn > Cu.

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, which indicates the diversity of their crystal lattice and metal–ligand bonding energies.

All the prepared complexes show similar solid-state IR spectra (Table 1) but they differ from the spectrum of the free acid. When the acid is converted to the salt, the absorption valency band of the C=O group, ν(C=O) at 1725 and 1695 cm^{-1}, disappears, wheras the bands of the asymmetric vibrations ν_{as}(OCO) at 1597–1635 cm^{-1} and of the symmetric vibrations ν_s(OCO) at 1324–1349 cm^{-1} are apparent. The IR spectra of the prepared complexes have broad absorption bands with a maximum at 3103–3457 cm^{-1}, confirming the presence of the lattice water. The values of the splitting for the absorption bands of the valency vibrations ν_{as}(OCO)

TABLE 1

Frequencies of characteristic absorption bands in IR spectra (cm^{-1}) and solubilities in water of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,2-dioxyacetates

Complex [a]	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu = (\nu_{as} - \nu_s)$	$\nu(OH)$	$\delta(CH_2)$ in $-CH_2COO$ group	C=C for 1,2-substituted	Solubility/ mol dm^{-3}
$CoL \cdot 15H_2O$	1623vs	1339s	284	3374s	1459s	1432s	4.40×10^{-2}
$NiL \cdot 30H_2O$	1597vs	1345s	252	3457s	1450s	1430s	5.70×10^{-2}
$CuL \cdot 8H_2O$	1635vs	1349s	286	3435s	1454s	1427s	3.90×10^{-5}
$ZnL \cdot 8H_2O$	1601vs	1324s	277	3103s	1456s	1422s	2.29×10^{-3}
$NaL \cdot 4H_2O$	1620vs	1345s	275	3405s	1450m	1435s	–

[a] Where L is $C_{10}H_8O_6^{2-}$.

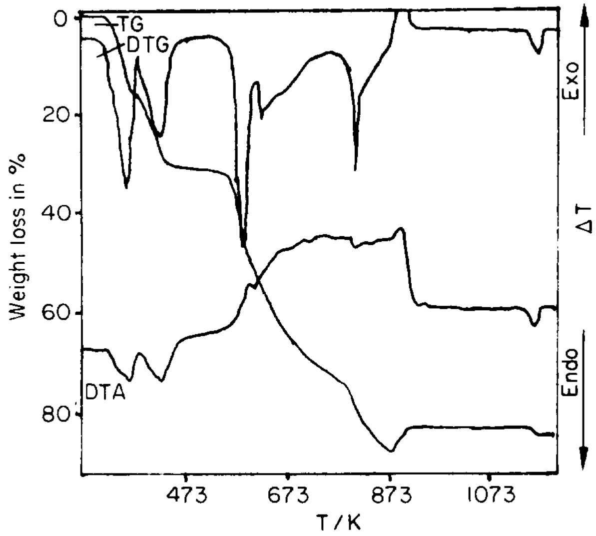

Fig. 2. TG, DTG and DTA curves of $CoC_{10}H_8O_6 \cdot 15H_2O$.

and $\nu_s(OCO)$ ($\Delta\nu = \nu_{as} - \nu_s$) are very high ($\Delta\nu = 252$–$286\,cm^{-1}$) and are similar to those in the sodium salt. The spectroscopic data suggest that the carboxylate group in the complexes studied is a bidentate bridging group.

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

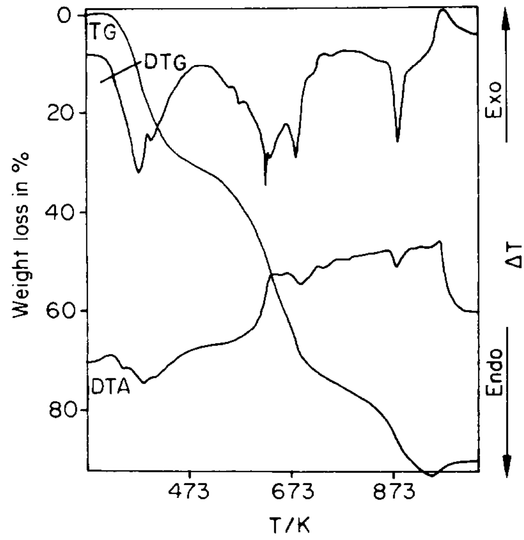

Fig. 3. TG, DTG and DTA curves of $NiC_{10}H_8O_6 \cdot 3OH_2O$.

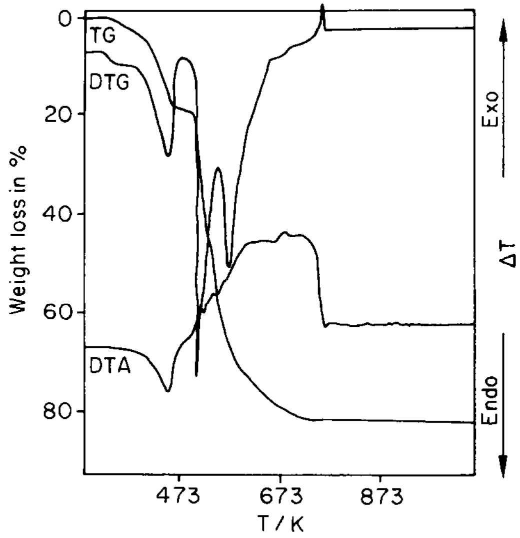

Fig. 4. TG, DTG and DTA curves of $CuC_{10}H_8O_6 \cdot 8H_2O$.

and Cu(II)) or two (Co(II) and Zn(II)) steps, forming hydrates at 473–493 K with fewer crystallization water molecules. Table 2 gives the ranges of the dehydration temperatures and the quantitative descriptions of the dehydration processes of the Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,2-dioxyacetates.

From the results, it can be suggested that the water crystallization molecules are bonded in different ways: with an anion (lost at 313–328 K); in the space lattice, hydrogen-bonded with an anion or an inner sphere

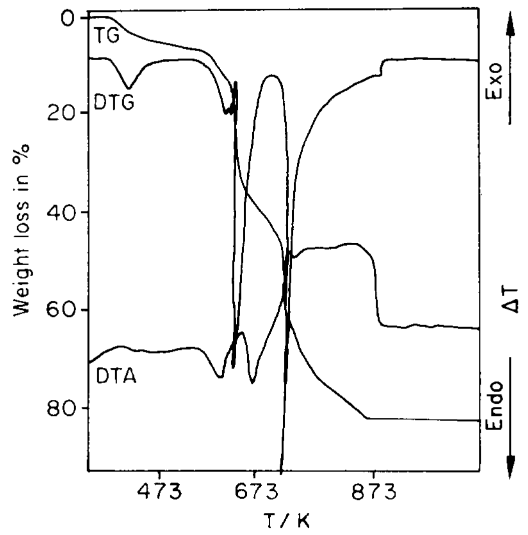

Fig. 5. TG, DTG and DTA curves of $ZnC_{10}H_8O_6 \cdot 8H_2O$.

TABLE 2

Data on the dehydration of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,2-dioxyacetates

Complex	Temp. range of dehydration I/K	Loss of weight in %		No. of H_2O moles lost	Temp. range of dehydration I/K	Loss of weight in %		No. of H_2O moles lost	Residue in %		Compounds
		Calc.	Found			Calc.	Found		Calc.	Found	
$CoL \cdot 15H_2O$	313–393	16.28	16.0	5	393–508	32.56	32.6	5	67.44	67.4	$CoL \cdot 5H_2O$
$NiL \cdot 30H_2O$	313–493	30.63	31.0	14	–	–	–	–	69.37	69.0	$NiL \cdot 16H_2O$
$CuL \cdot 8H_2O$	328–473	16.69	17.0	4	–	–	–	–	83.31	83.0	$CuL \cdot 4H_2O$
$ZnL \cdot 8H_2O$	318–446	6.23	6.4	1.5	545	12.45	12.8	1.5	87.54	87.2	$ZnL \cdot 5H_2O$

TABLE 3

Data for the decomposition of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,2-dioxyacetates

Complex	Temperatures of decomposition peaks (DTG)/K	Temp. of metal formation (DTG)/K	Loss of weight in %		Temp. of oxide formation/K	Residue in %	
			Calc.	Found		Calc.	Found
$CoL \cdot 5H_2O$	583, 625	808	10.65	10.4	908, 1171	14.20; 13.54	14.0; 13.8
$NiL \cdot 16H_2O$	618, 693	881	7.13	7.5	958	9.07	9.0
$CuL \cdot 4H_2O$	498, 563	–	–	–	733	18.43	18.5
$ZnL \cdot 5H_2O$	561, 661	–	–	–	848	18.77	18.4

water of the complexes (lost at 393–545 K, Co(II) and Zn(II)) [6]; and as coordination water which is strongly bonded with a metal ion (lost simultaneously with decomposition of the organic ligand). Comparing the final temperatures of the first and second steps of dehydration for the various complexes, the crystallization water molecules are bonded least strongly in the Zn(II) and Co(II) complexes; and the coordination water molecules are bonded most strongly in the Ni(II) and Co(II) complexes. The benzene-1,2-dioxyacetates of Co(II), Ni(II), Cu(II) and Zn(II) lose only some of their water molecules when heated and do not form anhydrous complexes.

When the partially dehydrated complexes were heated above 393–545 K (Table 3), they lost their last water molecules simultaneously with decomposition of the organic ligand. This process is accompanied by a strong exothermic effect, which is observed on the DTA curve and is connected with ignition of the decomposition products, carbon, and with oxidation of the metal to oxide (Co, Ni). On the DTG curves, these peaks are not observed during heating at 5 K min^{-1} and the decomposition products were not identified. During heating, the Co(II) and Ni(II) complexes decompose to the oxides (Co_3O_4, CoO, NiO), with intermediate formation of the free metals at 808 and 881 K, respectively; whereas the Zn(II) complex decomposes directly to the oxide.

The Cu(II) complex decomposes to CuO through, in all probability, intermediate formation of a mixture of free metal and Cu_2O (there is a strong peak on the DTG curve at 673 K). The oxidation of the free metal is accompanied by a strong peak on the TG curve.

The results indicate that the thermal decomposition of hydrated Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,2-dioxyacetates can be described in the following manner:

$$CoL \cdot 15H_2O \rightarrow CoL \cdot 10H_2O \rightarrow CoL \cdot 5H_2O \rightarrow Co \rightarrow Co_3O_4 \rightarrow CoO$$

$$NiL \cdot 30H_2O \rightarrow NiL \cdot 16H_2O \rightarrow Ni \rightarrow NiO$$

$$CuL \cdot 8H_2O \rightarrow CuL \cdot 4H_2O \rightarrow CuO$$

$$ZnL \cdot 8H_2O \rightarrow ZnL \cdot 6.5H_2O \rightarrow ZnL \cdot 5H_2O \rightarrow ZnO$$

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

In general, hydrated benzene-1,2-dioxyacetates, when heated in air, dehydrate in one or two steps losing some water molecules, and then decompose to the oxides, either directly (Zn) or with intermediate formation of the free metals (Co, Ni and probably Cu).

Comparing the temperatures of decomposition, it is possible to suggest that the stability of the complexes increases with increasing atomic number *Z* of the metal in the groups Co–Ni and Cu–Zn.

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