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THERMAL DECOMPOSITION OF COPPER(II) BENZENEDICARBOXYLATES

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The conditions and products of thermal decomposition of copper(II) benzenedicarboxylates in air atmosphere were studied at heating rates of 10 and 5 deg · min^{-1}. At a heating rate of 10 deg · min^{-1}, the o- and p-phthalate of copper(II) lose the crystallization water in two steps and the anhydrous complexes then decompose directly to CuO. Copper(II) m-phthalate loses crystallization water in one step to give the dihydrate, which then decomposes directly to CuO. When heated at 5 deg · min^{-1}, the m- and p-phthalates of copper(II) decompose in the same way, whereas the anhydrous o-phthalate decomposes to CuO through Cu_2O.

In recent years many papers have been published on copper(II) complexes with organic ligands. Complexes of copper(II) with o-phthalic acid have been studied by many authors. Herman [1] prepared the 1 : 1 copper(II) o-phthalate $2CuC_8H_4O_4 \cdot 9NH_3$, Borrows and Richtie [2] prepared $Na_2[Cu(C_8H_4O_4)_2] \cdot 2H_2O$ and Rayky [3] prepared $Na_2[Cu(C_8H_4O_4)_2 \cdot H_2O]$, in which the copper(II) has coordination number 6. Bobtelski et al. [4] used a titration method in aqueous alcoholic solution and found complexes of copper(II) with o-phthalic acid with metal to ligand ratios of 2 : 3 and 1 : 1; Vasiliev and Grochowski [5] determined their stability constants by polarography. Various complexes, have recently [6] been prepared by double decomposition between copper(II) sulphate and potassium o-phthalate at different temperatures. $Cu[C_8H_4(COO)COOH]_2 \cdot 2H_2O$ was prepared at room temperature, $Cu[C_8H_4O_4] \cdot H_2O$ at 80°, and $[Cu(C_8H_4O_4)]_2$ at 100°. The stability constants of copper(II) complexes with o-phthalic acid have been determined [7] by potentiometry. pH-metric titration revealed the presence of mixed copper(II) complexes [8] with o-phthalic acid and oxalic, malonic and fumaric acids and pyrocatechol. Studies were made on the system copper(II)—o-phthalic acid with dimethylsalicylic acid [9], ethylenediamine [10] and diaminepropane [11]. The formation of these complexes can be used for the extraction of copper(II) with organic solvents. The thermal stability of copper(II) o-phthalate in nitrogen atmosphere has been studied [12].

The salts of m- and p-phthalic acids are little known. A method of separation of Cu(II) from Ni and Co by using m-phthalic [13, 14] and p-phthalic acids [15] has been developed.

The aim of our work was to obtain o-, m- and p-phthalates of copper(II), and to examine their thermal decompositions during heating in air atmosphere.

Experimental

Copper(II) o-, m- and p-phthalates were prepared in double decomposition reactions by adding equivalent amounts of a 0.1 *M* solution of copper(II) nitrate to a hot solution of the ammonium salts of the phthalic acid (pH 5.5–5.7). The precipitates formed were heated at 333–343 K in the mother liquor for 0.5 h, then filtered off, washed with hot water to remove NH_4^+ and dried at 303 K to constant mass.

The contents of carbon and hydrogen were determined by elemental analysis. The contents of copper were determined from the TG curves, by ignition of the complexes to CuO and by polarography. The contents of crystallization water were determined thermogravimetrically and by isothermal heating of the complexes at given temperatures. The results are presented in Table 1.

Table 1 Analytical data

Copper(II) phthalate	Cu, %		C, %		H, %	
	calcd.	found	calcd.	found	calcd.	found
ortho-$CuC_8H_4O_4 \cdot 2.5H_2O$	23.30	23.3	35.22	35.3	3.30	3.0
meta-$CuC_8H_4O_4 \cdot 5H_2O$	20.00	19.3	30.22	29.5	4.40	4.2
para-$CuC_8H_4O_4 \cdot 2.5H_2O$	23.30	23.2	35.22	35.3	3.30	3.1

Table 2 Frequencies of absorption bands of COO^- ion and Cu–O bond in copper(II) benzenedicarboxylates (cm^{-1})

Complex		δH_2O	$\nu_{as}OCO$	$\nu_{sym}OCO$	$\Delta\nu$	ν_{Cu-O}
$CuL \cdot 2.5H_2O$*	(1, 2)**	3500–3350	1560	1420	140	410
$CuL \cdot 5H_2O$	(1, 3)	3600–3200	1560	1390	170	425
$CuL \cdot 2.5H_2O$	(1, 4)	3500–2800	1540	1420	120	420

* $L = C_6H_4(COO)_2^{2-}$

** position of COO^- groups on benzene ring

The IR spectra of the prepared complexes were recorded with a Specord 75 IR spectrophotometer over the range 4000–400 cm^{-1}. The samples were prepared as KBr discs.

The diffractograms of the copper(II) phthalates were recorded with a DRON–2 diffractometer with Ni-filtered CuK_α radiation over the range $2\Theta = 5–100°$ by the Debye–Scherrer method (Fig. 1).

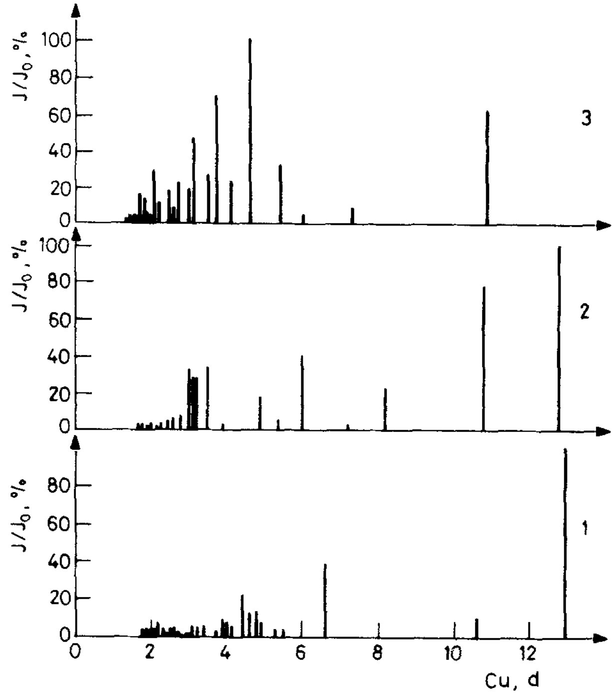

Fig. 1 X-ray diffractogram of copper(II): 1 – o-phthalate, 2 – m-phthalate, 3 – p-phthalate

The thermal stabilities of the complexes were studied by means of TG, DTG and DTA techniques. The measurements were made with an OD–102 derivatograph. The samples were heated in ceramic crucibles in air atmosphere at a heating rate of 10 or 5 deg·min^{-1} with a sensitivity TG = 200 mg. The results are presented in Tables 3 and 4 and Figs 2–4.

Table 3 Temperature ranges of dehydration and decomposition of copper(II) benzenedicarboxylates at a heating rate of 10 deg·min^{-1}

Complex		ΔT_1, K	H_2O, n	Loss of mass, %		ΔT_2, K	H_2O, n	Loss of mass, %		ΔT_3, K	Loss of mass, %		T_k, K
				calcd.	found			calcd.	found		calcd.	found	
$CuL \cdot 2.5H_2O$	(1, 2)	338–398	0.5	3.30	3.2	403–453	2	13.20	12.7	533–733	70.88	70.6	733
$CuL \cdot 5H_2O$	(1, 3)	333–468	3	17.00	17.0	—	—	—	—	533–798	75.00	74.7	798
$CuL \cdot 2.5H_2O$	(1, 4)	333–413	0.5	3.30	3.2	433–503	2	13.20	13.2	563–853	70.88	71.0	853

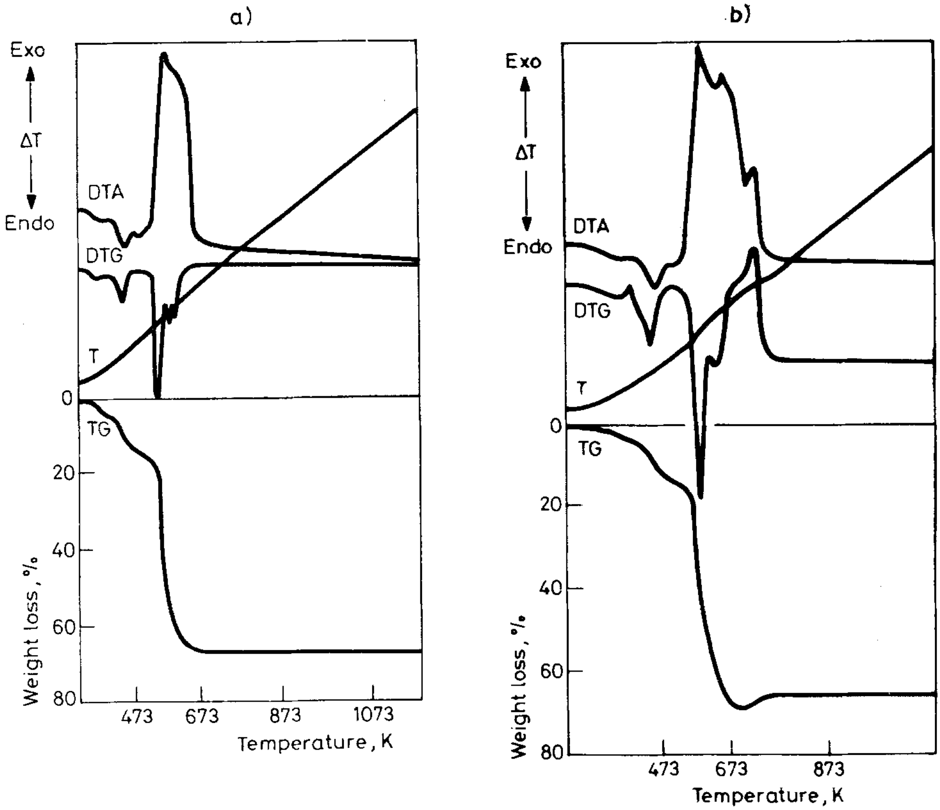

Fig. 2 TG, DTG and DTA curves of $CuC_8H_4O_4 \cdot 2.5H_2O$ (1, 2) at a heating rate a) 5 deg·min^{-1}, b) 10 deg·min^{-1}

Results and discussion

The benzenedicarboxylates of copper(II) were prepared as blue crystalline solids sparingly soluble in water. The results showed that the complexes of copper(II) with o-, m- and p-phthalic acids were prepared as hydrates with general formula $CuC_8H_4O_4 \cdot nH_2O$, where $n = 2.5$ for o- and p-phthalate and $n = 5$ for m-phthalate (Table 1).

Analysis of the IR spectra confirms the compositions of the complexes (Table 2). In the IR spectra of the copper(II) benzenedicarboxylates, broad absorption bands appear at 3600–3200 cm^{-1} and sharp bands at 1690–1590 cm^{-1}, confirming the presence of crystallization water in the outer sphere. The strong bands of the asymmetric (ν_{as}) and symmetric (ν_{sym}) vibrations of the COO^- group appear at

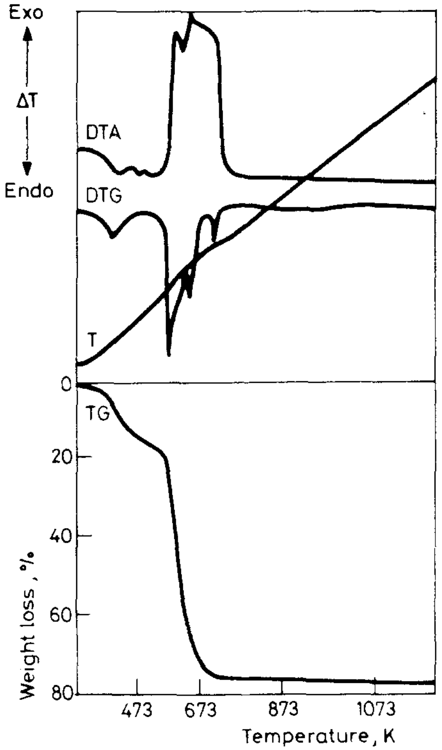

Fig. 3 TG, DTG and DTA curves of $CuC_8H_4O_4 \cdot 5H_2O$ (1, 3) at a heating rate 10 deg·min^{-1}

1560–1540 cm^{-1} and 1420–1390 cm^{-1}, respectively, and the bands of the Cu–O bond at 490–475 cm^{-1}. The largest separation between the frequencies due to the asymmetric and symmetric vibrations ($\Delta\nu = \nu_{as} - \nu_{sym}$) and the highest frequency of the absorption bands of the Cu–O bond were observed for copper(II) m-phthalate, which indicates a stronger metal-ligand interaction and a stronger deformation as compared to the o- and p-phthalates. $\Delta\nu$ has the lowest value for the p-phthalate; this is caused by the symmetrical structure of the ligand.

The recorded debyegrams showed that the o-, m- and p-phthalates of copper(II) are crystalline solids of low symmetry, with large unit cells and a high degree of crystallinity (Fig. 1). The degree of crystallinity decreases in the sequence:

o-phthalate > m-phthalate > p-phthalate

Copper(II) o-phthalate is readily soluble in water ($9.7 \cdot 10^{-3}$ mole·dm^{-3}), whereas the m- and p-phthalates are sparingly soluble in water ($5.3 \cdot 10^{-5}$ and $1.2 \cdot 10^{-5}$ mole·dm^{-3}, respectively). The differences in solubility are caused by the different structures of the complexes. In copper(II) o-phthalate the ligand is bidentate, coordinating through both carboxylic groups, whereas in the m- and p-phthalate complexes it is impossible because of the small ionic radius of copper(II) and the large distance between the carboxylic groups. Copper(II) o-phthalate presumably exists as a monomer, or preferably a dimer, but the m- and p-phthalates form macromolecules. The p-phthalate of copper(II) presumably has a linear structure. Concrete answers to these questions can be obtained only by determination of the full molecular structures of the complexes.

From the thermal curves of the copper(II) benzenedicarboxylates, the temperatures of dehydration and thermal decomposition were evaluated and are presented in Tables 3 and 4 and in Figs 2–4, where:

ΔT_1 and ΔT_2 = temperature ranges corresponding to the endothermic loss of a given number of crystallization water molecules (K),
$n H_2O$ = loss of nH_2O,
ΔT_3 = temperature range corresponding to decomposition of complexes to CuO (K),
T_k = temperature of CuO formation (K).

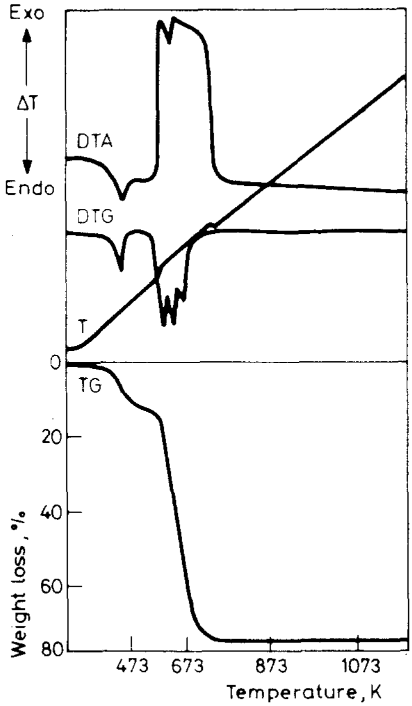

Fig. 4 TG, DTG and DTA curves of $CuC_8H_4O_4 \cdot 2.5H_2O$ (1, 4) at a heating rate 10 deg·min^{-1}

The results of thermal analysis demonstrated that the copper(II) benzenedicarboxylates decompose in various ways, depending on the rate of heating. At a heating rate of 5 deg·min^{-1}, copper(II) o-phthalate, $CuC_8H_4O_4 \cdot 2.5H_2O$, loses crystallization water in two steps. In the first step, at 338–393 K, it loses 0.5 water molecule; next, at 403–453 K, it loses the remaining 2 water molecules, yielding the anhydrous salt, which decomposes to CuO at 593–673 K (Fig. 2). During heating at 10 deg·min^{-1}, copper(II) o-phthalate is dehydrated in two steps. The anhydrous complex decomposes to Cu_2O at 533–733 K; above 733 K, oxidation occurs to CuO (Fig. 3).

When heated at 5 deg·min^{-1}, copper(II) m-phthalate pentahydrate loses 4 water molecules at 353–543 K. The monohydrate decomposes directly to CuO at 533–733 K (Table 4). During heating at 10 deg·min^{-1}, the pentahydrate loses 3 water molecules at 333–468 K and the dihydrate decomposes to CuO at 533–833 K (Fig. 3).

When heated at various heating rates, copper(II) p-phthalate decomposes in the same way. The hydrated complex undergoes dehydration in two stages, accompanied by two endothermic effects, and then decomposes exothermally, directly to CuO (Fig. 5).

The results suggest that the crystallization water in the studied complexes is bound in various ways: as outer and inner sphere water.

The thermal stability of the copper(II) benzenedicarboxylates increases in the sequence:

$$\text{o-phthalate} < \text{m-phthalate} < \text{p-phthalate}$$

Copper(II) p-phthalate is the most thermally stable and the most sparingly soluble of these complexes, which indicates the highest crystal lattice energy.

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Zusammenfassung — Die Umstände und Produkte der thermischen Zersetzung von Kupfer(II)-benzoldicarboxylaten wurden in Luftatmosphäre bei einer Aufheizgeschwindigkeit von 10 bzw. 5 grd/min untersucht. Bei einer Aufheizgeschwindigkeit von 10 grd/min geben Kupfer(II)-o- und p-phthalat ihr Kristallwasser in zwei Stufen ab, die wasserfreien Komplexe zerfallen anschliessend unmittelbar zu CuO. Kupfer(II)-m-phthalate geben Kristallwasser in einem Schritt ab und bilden dabei ein Dihydrat, was anschliessend direkt zu CuO zerfällt. Bei einer Aufheizgeschwindigkeit von 5 grd/min zeigt das m- und p-Phthalat des Kupfers(II) die gleichen Zersetzungserscheinungen, wogegen wasserfreies o-Phthalat sich zu CuO über die Zwischenstufe Cu_2O zersetzt.

Резюме — Условия и продукты термического разложения в атмосфере воздуха медных солей бензолдикарбоновых кислот были изучены при скоростях нагрева 10 и 5° в минуту. При скорости нагрева 10° в минуту соль о- и п-фталевой кислоты теряет кристаллизационную воду в две стадии, а образующиеся при этом безводные комплексы затем прямо разлагаются до оксида двухвалентной меди. м-Фталат меди теряет кристаллизационную воду в одну стадию, давая дигидрат, который затем разлагается с образованием оксида меди. При скорости нагрева 5° в минуту м- и п-фталаты меди разлагаются одиноковым образом, тогда как безводный о-фталат меди разлагается до окиси двухвалентной меди через стадию промежуточного образования окиси одновалентной меди.