

COMPLEXES OF DICAMBA WITH CADMIUM(II), COPPER(II), MERCURY(II), LEAD(II) AND ZINC(II) Synthesis and properties

A. Turek*, J. Kobyłecka and B. Ptaszyński

Institute of General and Ecological Chemistry, Technical University, 90-924 Łódź,
ul. Żeromskiego 116, Poland

Abstract

New solid complexes of a herbicide known as dicamba (3,6-dichloro-2-methoxybenzoic acid) with Pb(II), Cd(II), Cu(II) and Hg(II) of the general formula $M(\text{dicamba})_2 \cdot x\text{H}_2\text{O}$ (M =metal, $x=0-2$) and $\text{Zn}_2(\text{OH})(\text{dicamba})_3 \cdot 2\text{H}_2\text{O}$ have been prepared and studied. The complexes have different crystal structures. The carboxylate groups in the lead, cadmium and copper complexes are bidentate, chelating, symmetrical, in $\text{Hg}(\text{dicamba})_2 \cdot 2\text{H}_2\text{O}$ – unidentate, and in the zinc salt – bidentate, bridging, symmetrical. The anhydrous compounds decompose in three stages, except for the lead salt whose decomposition proceeds in four stages. The main gaseous decomposition products are CO_2 , CH_3OH , HCl and H_2O . Trace amounts of compounds containing an aromatic ring were also detected. The final solid decomposition products are oxychlorides of metals and CuO .

Keywords: dicamba complexes, IR spectra, mass spectrometry, thermal decomposition, X-ray diffractometry

Introduction

3,6-dichloro-2-methoxybenzoic acid (dicamba) is a selective translocatable herbicide, classified as 'auxin'. It is applied mainly for the control of annual and perennial broadleaved weeds in cereal crops [1]. Dicamba is usually used in mixture with other active substances, mainly with the derivatives of phenoxyalkanoic acids, such as 2,4D or MCPA. Dicamba is minimally absorbed to most soils, so it is easily transferred to the waters. However, it has been found that dicamba is adsorbed to some extent by organo-clays [2].

Dicamba has complexing properties, but relatively little research has been done on its complexes with metals. Complex salts of dicamba with calcium [3], manganese(II), cobalt(II) and zinc(II) [4] were obtained only by Smith, Kennard *et al.*, who also described some of their properties. The complexes of the formulae $M(\text{dicamba})_2 \cdot 5\text{H}_2\text{O}$ (M =Mn, Co, Zn) and $\text{Ca}(\text{dicamba})_2 \cdot 2\text{H}_2\text{O}$ were obtained as a result of the reaction of boiling aqueous alcoholic solution of dicamba with excess of the metal carbonate. The complexes of manga-

* Author for correspondence: E-mail: akturek@p.lodz.pl

nese, cobalt and zinc are isostructural, crystallize in monoclinic system and are readily soluble in water. The structure of the zinc salt was described in detail. The environment of the Zn^{2+} ion is octahedral. The coordination sphere of ZnO_6 consists of: (a) two oxygen atoms of the carboxylate groups, each from a different dicamba molecule ($-COO^-$ groups of the ligands are unidentate); these ligands are *cis*-related; (b) four oxygen atoms from the water molecules, two of these acting as bridges between adjacent complex units. The examination of the thermal decomposition of Zn(II), Co(II) and Mn(II) salts showed that four molecules of water (one lattice water, two *cis*-related coordinated waters and one of 'bridging' waters) are released at one stage at a relatively low temperature 30–90°C. The fifth water molecule, which is an element of the bridge, is released at the decomposition temperature of the complex (about 200°C). Taking these observations into consideration, the authors proposed for the dicamba complexes with Mn(II), Co(II) and Zn(II) the following molecular formula: $\{[M(dicamba)_2(H_2O)_3] \cdot 2H_2O\}_n$. The complex of dicamba with calcium, of the formula $[Ca(dicamba)_2(H_2O)_2]_n$, crystallizes in orthorhombic system. The calcium ion is eight-coordinated and surrounded by four oxygen atoms of the two bidentate, chelating $-COO^-$ groups, two oxygen atoms of the two unidentate, bridging $-COO^-$ groups and two oxygen atoms of the water molecules.

The present work is a part of a study on the properties of heavy metal complexes with herbicides of the phenoxyalkanoic group [5–8] and benzoic acid derivatives. It contains the synthesis, spectroscopic and thermal properties of new complexes of dicamba with bivalent cations of cadmium, zinc, copper, lead and mercury.

Experimental

Chemicals

Dicamba ($C_8H_6Cl_2O_3$, manufactured by 'Organika-Sarzyna' Poland) of purity 89.6%. Technical dicamba was purified by recrystallization from toluene. Pure dicamba melt at 112–115°C (theoretical melting point 114–116°C [1]).

$Zn(NO_3)_2 \cdot 4H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Hg(NO_3)_2 \cdot H_2O$ (Merck).

$CuCO_3 \cdot Cu(OH)_2 \cdot 0.5H_2O$, $PbCO_3$ (POCh Gliwice, Poland).

All salts used were analytically pure.

Synthesis of the complexes

To prepare complexes under study, 10^{-2} moles of dicamba and $5 \cdot 10^{-3}$ moles of metal salts were used. The final volume of solution was 50 mL. White Zn(II) and Cd(II) complexes were obtained by the evaporation of the solutions containing sodium 3,6-dichloro-2-methoxybenzoate and the metal nitrate at a dicamba/metal molar ratio 2:1. The sodium salt of dicamba was obtained by dissolving of the purified herbicide in NaOH (the final pH of the solution was about 7 [5]).

Cu(II) and Pb(II) complexes were obtained in the following way: a carbonate of the respective metal was dissolved in hot water – ethanol (*V/V* 1:1) dicamba solu-

tion [4] at a molar ratio L:M ~ 2:1, the mixture was kept close to the boiling point for about 10 min, then the remaining undissolved carbonate was filtered off and the filtrate was left to evaporate at room temperature. White lead and blue copper compounds were formed.

Hg(II) complex was synthesized in the following way: (1) dicamba was dissolved in NaOH to bring pH to about 8; (2) mercury(II) nitrate was dissolved in water with the addition of $1 \text{ mol dm}^{-3} \text{ HNO}_3$ (the acid prevented hydrolysis and precipitation of HgO); (3) mercury(II) nitrate solution was added dropwise while stirring, to the solution of the sodium salt of dicamba. The sparingly soluble white complex precipitated as soon as the reagents were mixed. The solution with the precipitate was left for 24 h.

The precipitates of thus synthesized complexes were collected by filtration, washed with a small amount of water and dried in air at room temperature. The yields of the Zn(II), Cd(II), Cu(II), Pb(II) and Hg(II) complexes were: 20, 45, 60, 65 and 75%, respectively.

Analysis of the complexes

The composition of the complexes was established on the basis of the analysis of the content of the metals, carbon and hydrogen (Table 1). Carbon and hydrogen were determined by elemental analysis (CHN analyser, Carlo Erba 1108), and zinc, cadmium, copper and lead by complexometric titration [9], after decomposition of the complexes with concentrated HNO_3 (UniClever BM-1z mineralizer, produced by Plazmatronika). To determine the content of mercury, a weighed sample of ~0.01 g was moistened with water and $1 \text{ mol dm}^{-3} \text{ NaOH}$ was added dropwise until the complex was completely decomposed (a clear yellow solution was formed). Next $1 \text{ mol dm}^{-3} \text{ HNO}_3$ was added dropwise until pH was ~7, and then 10 cm^3 of water was added. An excess of standard solution of EDTA, ammonium buffer and eriochrome black T as indicator were added to the solution and the excess of EDTA was titrated with standard solution of zinc(II) nitrate.

Water solubilities of the complexes at room temperature, established on the basis of the content of Cd(II), Cu(II), Pb(II) determined by complexometric method and Hg(II) by CV-AAS method in the saturated solutions, are: $1.22 \cdot 10^{-1}$, $3.13 \cdot 10^{-2}$, $1.16 \cdot 10^{-2}$ and $6.59 \cdot 10^{-5} \text{ mol dm}^{-3}$, respectively. The zinc complex is readily soluble in water.

Table 1 The results of the chemical analyses of the complexes

Compound	Metal/%		C/%		H/%	
	found	calcd.	found	calcd.	found	calcd.
$\text{Pb}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2$	32.34	32.01	29.71	29.67	1.75	1.55
$\text{Cu}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$	12.08	11.78	35.67	35.62	2.69	2.59
$\text{Cd}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 1.5\text{H}_2\text{O}$	18.54	19.40	33.07	33.16	2.22	2.24
$\text{Hg}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$	29.45	29.66	29.44	28.39	2.01	2.06
$\text{Zn}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2$	15.02	15.50	34.21	34.16	2.49	2.37
$\text{Zn}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)(\text{OH}) \cdot 2\text{H}_2\text{O}$						

X-ray, IR and thermal analyses

Powder X-ray diffraction patterns of dicamba and its complexes with metals under study were recorded on Siemens D 5000 diffractometer, using $\text{CuK}\alpha$ radiation monochromatized by means of a secondary graphite monochromator, within the 2θ range $2\text{--}90^\circ$ (Fig. 1).

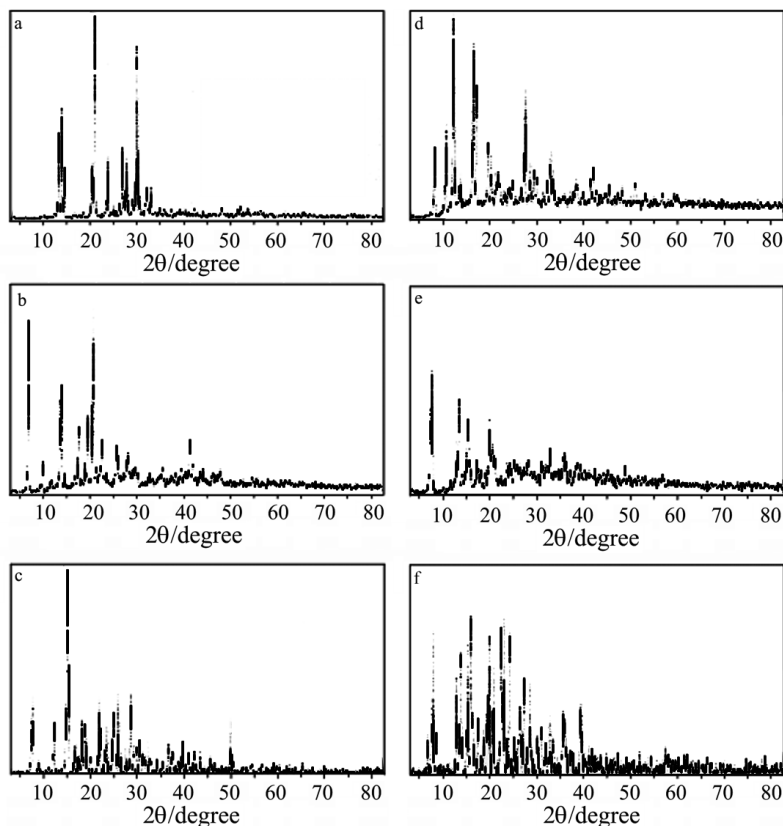


Fig. 1 X-ray diffraction patterns of: a – dicamba (HL), b – $\text{HgL}_2 \cdot 2\text{H}_2\text{O}$, c – $\text{CdL}_2 \cdot 1.5\text{H}_2\text{O}$, d – $\text{CuL}_2 \cdot 2\text{H}_2\text{O}$, e – PbL_2 , f – $\text{ZnL}_2 \cdot \text{Zn}(\text{OH})\text{L} \cdot 2\text{H}_2\text{O}$

IR spectra of the sodium salt of dicamba and the dicamba complexes were recorded on a FITR-8501 spectrometer (Shimadzu), within frequency range $4000\text{--}400\text{ cm}^{-1}$, in KBr disc (Table 2).

The TG, DTG and DTA curves of the complexes under study were recorded on OD-102/1500 derivatograph. The samples of 100 mg placed in corundum crucible were heated in air atmosphere over the temperature range $20\text{--}1000^\circ\text{C}$, with heating rate 10° min^{-1} (Table 3 and Fig. 2). As reference Al_2O_3 was used. For the characterization of gaseous products of thermal decomposition of cadmium, copper, lead and

Table 2 Vibration frequencies of the carboxylate and ether groups in the complexes of dicamba

Compound	Vibration of the -COO group		Vibration of the Ar-O-C group		
	$\nu_{\text{asym}}/\text{cm}^{-1}$	$\nu_{\text{sym}}/\text{cm}^{-1}$	$\Delta=\nu_{\text{asym}}/\text{cm}^{-1}-\nu_{\text{sym}}/\text{cm}^{-1}$	$\nu_{\text{asym}}/\text{cm}^{-1}$	$\nu_{\text{sym}}/\text{cm}^{-1}$
$\text{NaC}_8\text{H}_5\text{Cl}_2\text{O}_3$	1603	1404	199	1238	1180
$\text{Pb}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2$	1526	1406	120	1238	1180
$\text{Cu}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$	1541	1406	135	1234	1182
$\text{Cd}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 1.5\text{H}_2\text{O}$	1591	1410	181	1236	1184
$\text{Hg}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$	1605	1400	205	1236	1182
$\text{Zn}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot \text{Zn}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)(\text{OH}) \cdot 2\text{H}_2\text{O}$	1653	1558	145	1236	1180
	1647	1541			
	1636	1508	78		

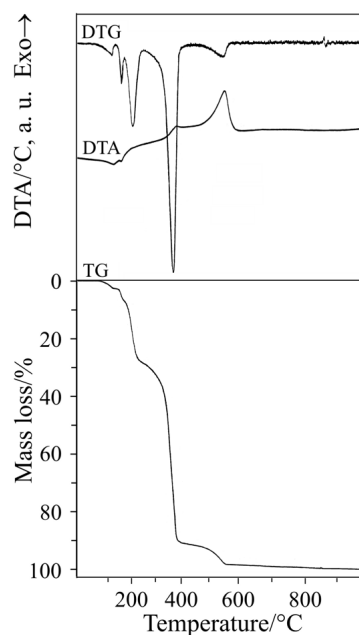


Fig. 2 Thermal analysis curves of $\text{Hg}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ (sample mass 100 mg)

zinc complexes TG/DTA-SET SYS-16/18 thermoanalyser connected with a ThermoStar mass spectrometer (Balzers) was used. The mass of the samples placed in platinum crucibles were 11.88, 6.91, 8.56 and 14.72 mg, respectively. The measurements were carried out in the conditions the same as above with flow rate of air $30 \text{ cm}^3 \text{ min}^{-1}$ and ion source temperature 1500°C . The results of the thermal analysis are presented in Table 4 and Figs 3, 4.

Results and discussion

New complexes of dicamba with cadmium(II), copper(II), lead(II) and mercury(II) of the general formula $\text{M}(\text{dicamba})_2 \cdot x\text{H}_2\text{O}$ (where $x=0-2$) and $\text{Zn}_2(\text{OH})(\text{dicamba})_3 \cdot 2\text{H}_2\text{O}$ were synthesized and examined. All these complexes precipitated in the form of powders.

Water solubility of the complexes (293K) decreases in the following order: $\text{Zn} \gg \text{Cd} > \text{Cu} \sim \text{Pb} \gg \text{Hg}$. The solubility of Zn(II) compound with dicamba is high, which probably is the cause of the difficulties in its synthesis. Although the literature provides the description of the structure of $\text{Zn}(\text{dicamba})_2 \cdot 5\text{H}_2\text{O}$ [4], we were not able to repeat its synthesis. In all attempts to obtain it, the ratio between Zn and the ligand in the compound synthesized was always 2:3.

The powder diffraction patterns showed that the complexes are crystalline and have different structures.

Table 3 Thermal analysis data of dicamba complexes (mass sample 100 mg)

Compound	Stage	Temperature range of decomposition stage/°C	Mass loss/%	Thermal effects and temperature of peaks/°C
$\text{Pb}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2$	I	230–300	36.0	240, 260 exo
	II	300–420	15.0	360 exo
	III	420–600	10.0	540 exo
	IV	600–1000	31.0	–
$\text{Cu}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$	D	80–160	6.5	130 endo
	I	160–390	53.5	broad exo
	II	390–620	26.0	520, 600 exo
	III	620–740	9.0	broad exo
$\text{Cd}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 1.5\text{H}_2\text{O}$	D	100–180	4.5	150 endo
	I	230–300	30.0	broad exo
	II	300–480	38.0	380 exo
	III	480–740	24.0	560, 720 endo
$\text{Hg}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$	D	80–160	6.5	110, 150 endo
	I	160–240	21.0	–
	II	240–400	63.0	380 exo
	III	400–570	9.0	550 exo
$\text{Zn}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot \text{Zn}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)(\text{OH}) \cdot 2\text{H}_2\text{O}$	D	60–140	6.5	140 endo
	I+II	230–400	58.0	broad exo
	III	400–600	23.5	520 exo

D-dehydration

Table 4 Gaseous products of thermal decomposition of the dicamba complexes

Stage of decomposition	<i>m/z</i>	Cu	Cd	Zn	Pb	
Dehydration	17	OH ⁺	OH ⁺	OH ⁺	–	
	18	H ₂ O ⁺	H ₂ O ⁺	H ₂ O ⁺	–	
	31	OCH ₃ ⁺	–	–	–	
	12	C ⁺	C ⁺	C ⁺	C ⁺	
	15	CH ₃ ⁺	CH ₃ ⁺	CH ₃ ⁺	CH ₃ ⁺	
	17	OH ⁺	OH ⁺	OH ⁺	OH ⁺	
	18	H ₂ O ⁺	H ₂ O ⁺	H ₂ O ⁺	H ₂ O ⁺	
	31	OCH ₃ ⁺	OCH ₃ ⁺	OCH ₃ ⁺	OCH ₃ ⁺	
	I	35, 37	Cl ⁺	Cl ⁺	Cl ⁺	Cl ⁺
		44, 45, 46	CO ₂ ⁺	CO ₂ ⁺	CO ₂ ⁺	CO ₂ ⁺
78		C ₆ H ₆ ⁺	C ₆ H ₆ ⁺	C ₆ H ₆ ⁺	C ₆ H ₆ ⁺	
108		–	C ₆ H ₅ OCH ₃ ⁺	–	–	
113		–	C ₆ H ₅ Cl ⁺	C ₆ H ₅ Cl ⁺	–	
126		–	C ₆ H ₄ ClCH ₃ ⁺	C ₆ H ₄ ClCH ₃ ⁺	–	
161		C ₆ H ₃ Cl ₂ CH ₃ ⁺	C ₆ H ₃ Cl ₂ CH ₃ ⁺	C ₆ H ₃ Cl ₂ CH ₃ ⁺	C ₆ H ₃ Cl ₂ CH ₃ ⁺	
12		C ⁺	C ⁺	C ⁺	C ⁺	
15		–	–	CH ₃ ⁺	–	
17		OH ⁺	OH ⁺	OH ⁺	OH ⁺	
II	18	H ₂ O ⁺	H ₂ O ⁺	H ₂ O ⁺	H ₂ O ⁺	
	31	–	OCH ₃ ⁺	OCH ₃ ⁺	OCH ₃ ⁺	
	35, 37	Cl ⁺	Cl ⁺	Cl ⁺	Cl ⁺	
	44, 45, 46	CO ₂ ⁺	CO ₂ ⁺	CO ₂ ⁺	CO ₂ ⁺	
	78	–	C ₆ H ₆ ⁺	C ₆ H ₆ ⁺	–	
	94	C ₆ H ₅ OH ⁺	–	–	–	
	108	–	–	–	–	
	113	–	C ₆ H ₅ Cl ⁺	C ₆ H ₅ Cl ⁺	–	
	126	–	C ₆ H ₄ ClCH ₃ ⁺	C ₆ H ₄ ClCH ₃ ⁺	–	
	129	C ₆ H ₄ OHCl ⁺	–	–	–	
III	161	–	C ₆ H ₃ Cl ₂ CH ₃ ⁺	C ₆ H ₃ Cl ₂ CH ₃ ⁺	–	
	35, 37	Cl ⁺	Cl ⁺	Cl ⁺	Cl ⁺	
IV	35, 37	–	–	–	Cl ⁺	

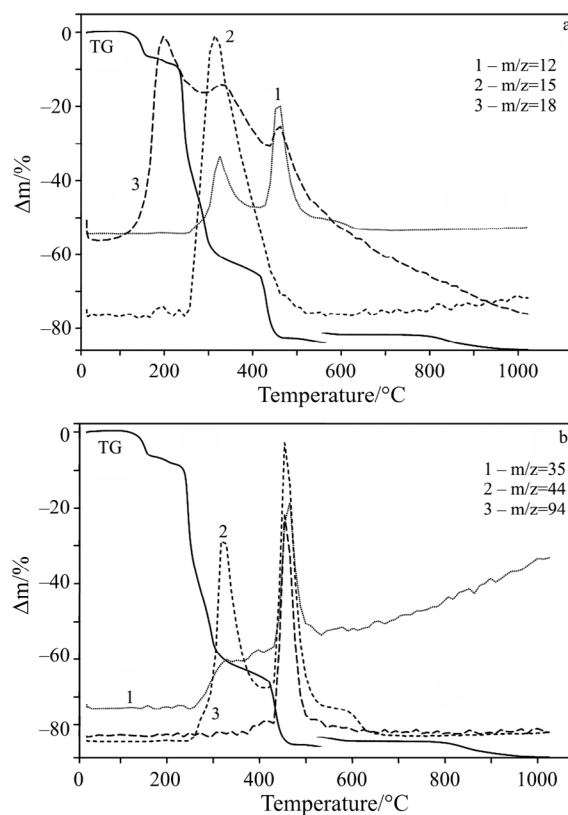


Fig. 3 TG curve of $\text{Cu}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ and ion current detected by MS for: a – $m/z=12, 15, 18$; b – $m/z=35, 44, 94$

The results of structural studies published by Smith and Kennard show that the carboxylate group in the complexes of metals with dicamba is either unidentate (Mn(II), Zn(II) and Co(II) complexes [4]) or bidentate bridging and chelating (in the Ca(II) salt [3]). Monocrystals of the complexes under study have not been hitherto obtained, so the type of the metal-carboxylate group bond has been identified on the basis of the IR spectroscopic analysis. The following factors have been taken into consideration: (a) the position of the bands of the characteristic vibrations of the dissociated carboxylate group $\nu(\text{OCO})_{\text{asym}}$ and $\nu(\text{OCO})_{\text{sym}}$; (b) the value of the split of these bands $\Delta\nu = \nu_{\text{asym}} - \nu_{\text{sym}}$ and (c) the direction of their shifts in relation to carboxylate group bound by an ionic bond [10, 11]. Table 2 presents the frequencies of the valence vibrations of the carboxylate group of the complexes and, for comparison, the frequencies of vibrations ν_{asym} and ν_{sym} in the sodium salt of dicamba, which, as it is assumed, contains the $-\text{COO}^-$ group with an ionic bond. The IR spectra of Na-dicamba and $\text{M}(\text{dicamba})_2 \cdot x\text{H}_2\text{O}$ complexes exhibit single peaks, while in the spectrum of the zinc complex a split is observed in the bands of the asymmetric and symmetric vibrations of

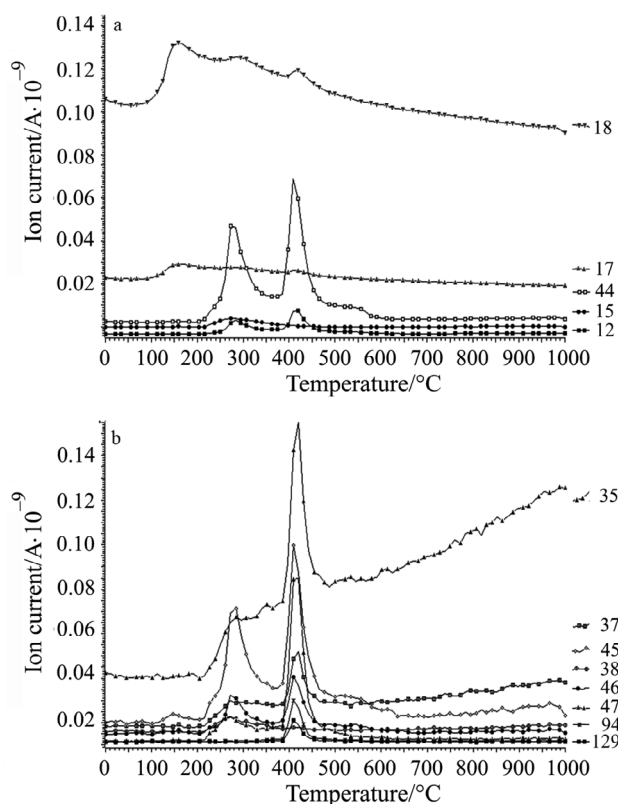


Fig. 4 Ion current vs. temperature for $\text{Cu}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ (sample mass 6.91 mg, heating rate $10^\circ\text{C min}^{-1}$): a – $m/z=12, 15, 17, 18, 44$; b – $m/z=35, 37, 38, 45, 46, 47, 94, 129$

the $-\text{COO}^-$ group. The frequencies of vibrations ν_{asym} and ν_{sym} in the cadmium, copper and lead complexes are shifted towards lower and higher values, respectively, in comparison with the ionic bond, and the values of Δ are lower than those calculated for Na-dicamba. This may indicate the presence of bidentate, symmetric chelating $-\text{COO}^-$ groups in these complexes. In the case of the mercury salt the value of ν_{asym} is slightly higher, and that of ν_{sym} – lower than the frequencies characteristic of Na-dicamba. The value of Δ for $\text{Hg}(\text{dicamba})_2 \cdot 2\text{H}_2\text{O}$ is by 6 cm^{-1} higher than for the sodium salt. These data indicate the presence of unidentate $-\text{COO}^-$ groups in the Hg complex. The most complex IR spectrum is observed for the Zn salt. ν_{asym} and ν_{sym} bands are split and, compared with the sodium salt, shifted towards higher frequencies, which, together with low Δ values, could indicate the presence of bidentate symmetric bridging $-\text{COO}^-$ groups. On the other hand, the split of the valence vibration bands may be caused by the occurrence of two types of $-\text{COO}^-$ group coordination.

Thermal analysis data of the examined complexes are listed in Table 3 and the TG, DTG, DTA curves for $\text{Hg}(\text{dicamba})_2 \cdot 2\text{H}_2\text{O}$ are presented in Fig. 2. As the complexes un-

der study are heated, the hydrated complexes of Cu(II), Cd(II) and Zn(II) are first dehydrated in a one-stage process, while Hg(II) complex loses water in two stages. The DTA curves show endothermic peaks corresponding with these processes. In the case of the zinc salt, apart from water hydroxyl group is also dissociated. The dehydration of the four complexes takes place within the temperature range of 80°C. Their thermal stability determined on the basis of the temperature of the beginning of their dehydration (Table 3) increases in the following order: Zn<Cu~Hg<Cd.

The decomposition of anhydrous salts of Cu(II), Cd(II), Hg(II) and Zn(II) proceeds in three overlapping stages, involving continuous mass losses. In the case of Pb(II) complex, which does not contain water, four stages of decomposition were identified. The thermal stability of the anhydrous Cu(II) and Hg(II) compounds (the decomposition starts at 160°C) is lower than that of Zn(II), Cd(II) and Pb(II) complexes (whose decomposition begins at 230°C). The summary thermal effects of the decomposition are exothermic. Small endothermic peaks were only observed on the DTA curve of the cadmium salt in the third stage of its decomposition. The decomposition of the zinc complex ends at 600°C, and the decomposition of cadmium and copper salts – at 740°C. The final solid decomposition products, identified by the diffractometric analysis [12], are zinc and cadmium oxychlorides and copper(II) oxide. A further slight loss in mass is probably associated with gradual evaporation of the above mentioned compounds or formation slight amounts of other decomposition products, which could not be identified by X-ray powder diffractometry. The decomposition of the lead complex involves a continuous loss of the mass up to 1000°C. Since at higher temperatures the sinters of the complex melt into the crucible material, it was impossible to carry out the diffractometric analysis of its final decomposition products. In the case of the mercury salt the loss in mass was 100% already at 550°C. Due to the rapid decomposition of the complex no sinters were obtained, which could have allowed to identify intermediate solid products of the thermolysis. At 1000°C the loss of the mass of the complexes of Zn and Cu is 92% and of Cd and Pb – 98%.

Mass spectra of the gaseous products of decomposition of Zn(II), Cd(II), Cu(II) and Pb(II) complexes were recorded. The mass spectra and the curve of Cu(II) complex are presented in Figs 3 and 4. Table 4 presents the identified volatile products formed in the course of the decomposition of the four complexes. H₂O⁺ is of course a volatile product of the dehydration stage, but it is remarkable that in the case of Cu(II) complex the presence of an OCH₃⁺ ion was also observed. This was in agreement with the derivatographic analysis (Table 3), which showed that the thermal stability of the anhydrous Cu(II) complex is lower than the stability of the complexes of Cd(II), Zn(II) or Pb(II). The gaseous products of individual stages of the thermal decomposition are different, but certain tendencies can be observed, including the fact that after the dehydration stage, CH₃⁺, OCH₃⁺, Cl⁺ ions are released and the combustion of the organic substance starts, which causes the release of high amounts of CO₂. The process occurs in the first and second decomposition stages. In the case of Cd(II) and Zn(II) complexes the release of carbon dioxide is accompanied by the appearance of small amounts of many chloro- and methyl- derivatives of benzene. The number of the derivatives is considerably smaller in the case of Pb(II) and Cu(II) complexes, and in the case of Cu(II) complex phenol derivatives occur instead. High

amounts of Cl^+ are released in the final stage of decomposition of all the complexes, which may imply the decomposition of metal oxychlorides whose presence was found in the course of the diffractometric analysis of the sinters of Cd(II) and Zn(II) complexes. As the final mass losses are very large, it is probable that gaseous metal compounds also evaporate.

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