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**Complexes of Zinc (II) with *o*-Methyl-, *o*-Hydroxy-
and *o*-Chlorobenzoic Acid**

Kompleksy cynku (II) z kwasem *o*-metylo, *o*-hydroksy i *o*-chlorobenzoesowym

Zinc (II) complexes with aromatic compounds are little known. *o*-Hydroxybenzoate of zinc (II) was prepared in solid state as anhydrous compound [1, 2], di- [3] and trihydrated ones [4-5]. It was found that trihydrated complex crystallizes in monoclinic system in space group $C 2n$ [5] and has luminescence properties [6]. Zinc (II) *o*-chlorobenzoate crystallizes also in monoclinic system [7]. It is used in photographic technics for preparing the light-sensitive materials [8-10].

The aim of our work was to obtain zinc (II) *o*-methylbenzoate, *o*-hydroxybenzoate and *o*-chlorobenzoate and examine their physico-chemical properties.

EXPERIMENTAL

PREPARATION OF COMPLEXES

Zinc (II) *o*-methylbenzoate, *o*-hydroxybenzoate and *o*-chlorobenzoate were prepared by adding equivalent quantities of 0.1 M solution of ammonium *o*-methyl-, *o*-hydroxy- or *o*-chlorobenzoate (pH 4.5-5.0) to a hot 0.2 M solution of zinc (II) nitrate, followed by crystallization on a water bath at 333-343 K.

The precipitate formed was filtered off, washed with distilled water to remove NH_4^+ ions and dried at 303 K to constant weight.

ANALYTICAL DATA

The content of carbon and hydrogen in complexes prepared was determined on the basis of elemental analysis by using V_2O_5 as oxidizing agent. The content of chlorine was determined by Schöniger method [11] and zinc (II) — by ignition of the preparations to ZnO at 1273 K or from TG curves. The water contents were determined from TG curves. The results obtained are presented in Table 1.

IR SPECTRA AND DIFFRACTOGRAMS

IR spectra of *o*-methyl-, *o*-hydroxy- and *o*-chlorobenzoic acid, their compounds with zinc (II) and sodium were recorded. The measurements were made on a UR-20 spectrophotometer within the range from 4000–400 cm^{-1} . The samples were prepared as KBr discs.

The diffractograms of prepared complexes were recorded on a DRON-2 diffractometer by using $\text{CuK}\alpha$ (Ni filtered) radiation. The measurements were made by the Debye—Scherrer method over the range $2\Theta = 5^\circ\text{--}80^\circ$. The results are presented in Fig. 1.

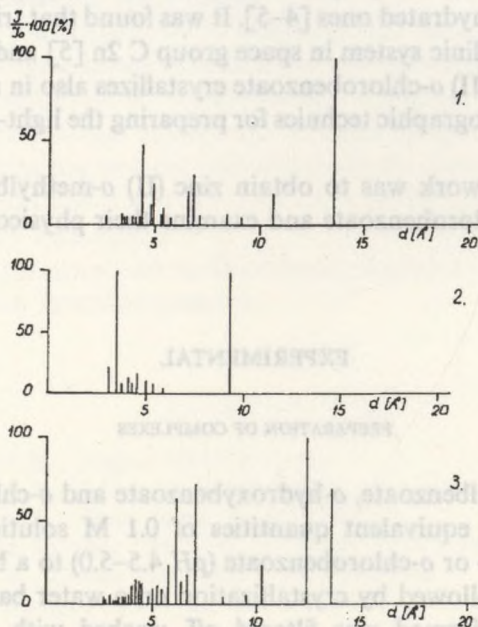


Fig. 1. Radiograms of 1. *o*-hydroxybenzoate, 2. *o*-chlorobenzoate, *o*-methylbenzoate of zinc (II)

DETERMINATION OF SOLUBILITY

The solubilities in water of obtained complexes at 303 K were determined. The saturated solutions of salts were obtained and 10 cm³ samples were taken out. The content of zinc (II) in the samples was determined by using polarographic method. The measurements were made on a polarograph OH-102 (Radelkis). On the basis of 3–4 results the solubilities of complexes were determined.

DERIVATOGRAPHIC MEASUREMENTS

The thermal stability of complex obtained was studied. The curves of TG, DTG and DTA were recorded. The measurements were made on an OD-102 derivatograph at heating rate 5 and 10 deg·min⁻¹ at sensitivity TG = 100 mg, DTG—1/5 and DTA—1/10. The samples of 100 mg were heated in air atmosphere in ceramic crucibles to 1273 K. Al₂O₃ was used as a standard.

RESULTS AND DISCUSSION

Zinc (II) *o*-methylobenzoate and *o*-chlorobenzoate were prepared as white colored solids sparingly soluble in water. On the basis of elemental analysis (Table 1) it has been found that zinc (II) *o*-methylobenzoate and *o*-hydroxybenzoate are anhydrous complexes with the ratio of metal to ligand 1:2, and *o*-chlorobenzoate is nanohydrated salt with the ratio of metal to ligand 1:2.

IR spectra of complexes obtained, and for comparison, of maternal acids and their sodium salts, were recorded. An analysis of spectra confirms the composition of complex. An analysis of the IR spectra confirms the composition of complexes. In the IR spectra of zinc (II) complexes the obtained bands characteristic of COOH in *o*-methyl-, *o*-hydroxy- and chlorobenzoic acid disappear at 1650, 1680 and 1695 cm⁻¹, respectively, which indicates that hydrogen atom in the COOH group is substituted by zinc ion. In the IR spectra of complexes, the absorption bands of asymmetric (ν_{as}) and symmetric (ν_s) vibrations of COO⁻ group appear at 1530–1540 cm⁻¹ and 1380–1445 cm⁻¹, respectively (Table 2).

In the spectrum of zinc (II) *o*-chlorobenzoate strong broad absorption band appear with max, at 3450 cm⁻¹ and sharp band at 1635 cm⁻¹, confirming the presence of crystallization water, and the band at 710–740 cm⁻¹ characteristic of C—Cl vibrations (ν_{Cl}). The bands characteristic of crystallization water are not observed in the IR spectra of zinc (II) *o*-methyl- and *o*-hydroxybenzoate, which confirms the anhydrous character of salts.

Table 1. Analytical data

Complex	% Zn		% C		% H		% Cl		Solubility [mol·dm ⁻³]
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
Zn(C ₆ H ₄ (CH ₃)COO) ₂	18.48	18.32	54.30	53.96	4.52	3.98	—	—	5.62·10 ⁻⁴ 348
Zn(C ₆ H ₄ (OH)COO) ₂	14.25	19.25	49.52	48.96	2.95	2.48	—	—	6.10·10 ⁻⁶ 220
Zn(C ₆ H ₄ ClCOO) ₂ ·9H ₂ O	15.18	15.20	39.05	40.08	3.25	3.85	16.49	17.02	5.21·10 ⁻⁵ 238

Table 3. Thermal data on decomposition of zinc (II) *o*-methyl-, *o*-hydroxy and *o*-chlorobenzoate in air atmosphere

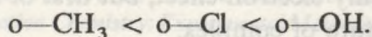
Complex	Melting point [K]	T ₁ [K]	Peak temp. of DTG	Loss of weight [%]		Product of decomposition	T ₂ [K]	Loss of weight [%]		Effects
				Calcd	Found			Calcd	Found	
Zn(C ₆ H ₄ (CH ₃)COO) ₂	523	573–773	733	62.68	62.00	ZnCO ₃	773–1053	75.74	76.00	endo 523.753 exo 953
Zn(C ₆ H ₄ (OH)COO) ₂	—	503–793	773	40.06	40.00	Zn(C ₆ H ₄ (O)COO)	673–993	76.02	76.00	endo 563.753 exo 953
Zn(C ₆ H ₄ ClCOO) ₂ ·9 H ₂ O	503	558–648 648–848	673 838	57.70 79.80	58.00 79.00	Zn ₂ O(C ₆ H ₄ ClCOO) ₂ Zn ₂ O·ZnCl ₂	848–950	84.89	85.00	endo 503.000 exo 643 838

T₁ — temperature range of decomposition of complex to intermediate product; T₂ — temperature range of decomposition to ZnO; T_k — temperature of ZnO formation

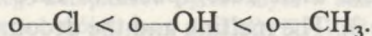
Table 2. Frequencies of absorption bands of characteristic groups of zinc (II) and sodium *o*-methyl-, *o*-hydroxy- and *o*-chlorobenzoates [cm^{-1}]

Complex	$\nu_{as} \text{COO}^-$	$\nu_s \text{COO}^-$	$\Delta\nu \text{COO}$	νCl	νOH	$\nu \text{ZN—O}$
$\text{Zn}(\text{CH}_3\text{C}_6\text{H}_7\text{COO})_2$	1530	1445	85	—	—	480
$\text{CH}_3\text{C}_6\text{H}_4\text{COONa}$	1555	1407	148	—	—	—
$\text{Zn}(\text{HOC}_6\text{H}_4\text{COO})_2$	1530	1380	150	—	1460	450
$\text{HOC}_6\text{H}_4\text{COONa}$	1582	1378	204	—	1480	—
$\text{Zn}(\text{ClC}_6\text{H}_4\text{COO})_2 \cdot 9\text{H}_2\text{O}$	1540	1410	130	710–740	—	430
$\text{ClC}_6\text{H}_4\text{COONa}$	1570	1385	185	710–740	—	—

The bands of asymmetric vibrations of COO^- are displaced to lower frequencies and the bands of symmetric vibrations — to higher ones compared with suitable bands of sodium salts which permits to suggest that COO^- group is bidentate chelating [12, 13]. The magnitudes of separation between frequencies due to asymmetric and symmetric vibrations of COO^- group ($\Delta\nu = 85\text{--}150 \text{ cm}^{-1}$) (Table 2) for prepared complex are notably smaller than for respective compounds of sodium ($\Delta\nu = 148\text{--}204 \text{ cm}^{-1}$). This is a result of a stronger action of Zn (II) ion than of Na (I) one on a ligand, stronger deformation and smaller degree of ionic bond in complexes studied than in sodium salts. This fact confirms also bidentate chelating character of ligands. The magnitude of separation $\Delta\nu \text{COO}$ for complexes prepared increases in the order:



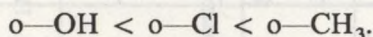
which indicates the increasing complex stability [12, 13, 14]. The bands of OH group vibrations in the IR spectra of zinc (II) *o*-hydroxybenzoate are insignificantly displaced compared with the respective bands of sodium salt ($\Delta\nu = 20 \text{ cm}^{-1}$). On this basis it is possible to suggest that OH group does not take part in the metal-ligand coordination. The frequencies of absorption band of zinc oxygen bond (Table 2) increase in the order:



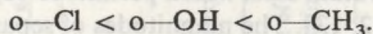
According to Burger [14] magnitude of the M—O stretching frequencies and that of the stability constants of the complexes change in the same direction. This is to be expected since an innerbase in the M—O bond order means higher stability of complex. In the cases where no equilibrium measurements are

available, these infrared data may be indicative of the stability of the complexes. However, in view of the fact that conjugation of the M—O, C—O and C—C bands may occur in chelate rings of these complexes, and, hence, there will be no "pure" M—O-stretching vibration, only M—O vibrations of completely analogous complexes can be compared for the purpose of obtaining information on the stability of the complexes.

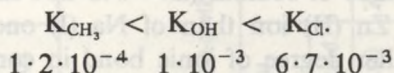
In order to confirm the crystalline structure of prepared complexes the diffractograms were recorded (Fig. 1). It has been found that zinc (II) *o*-benzenecarboxylates are crystalline compounds of low symmetry and big unit cells and their crystallinity degree ($\alpha = \sum_{n=5}^{\infty} 1$) increases in the order:



Zinc (II) *o*-benzenecarboxylates are sparingly soluble in water. Their solubilities are of the order 10^{-4} – 10^{-6} mol·dm⁻³ and increase in the order:

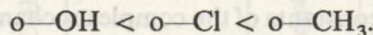


Contrary to the dissociation constants of acid



It is necessary to take into account that in the case of substituent in ortho position, the influences on the character, bond strength, and the charge of COO⁻ group has not only electron effect, but first of all, steric effect and also one solvation and structure of complex.

The thermal stability of complexes prepared was studied. On the basis of thermal curves temperatures and products of decomposition were determined (Table 3). Zinc (II) carboxylates under study, when heated in air, decompose in two or three steps. Anhydrous zinc (II) *o*-methylbenzoate heated is melted at 523 K and next undergoes to ZnO with intermediate formation unstable ZnCO₃. Anhydrous zinc (II) *o*-hydroxybenzoate decomposes to Zn(C₄H₄(O)COO) which is converted to ZnO. Hydrated zinc (II) *o*-chlorobenzoate melts at 503 K and then decomposes to ZnO forming unstable intermediate products (Table 3). The melting and the decomposition temperatures of complexes obtained increase in the order:



The thermal study confirms the results obtained on the basis of the analysis of the IR spectra.

Zinc (II) oxide, which is the last product of thermal decomposition of the complexes is formed in different temperatures. The temperature of ZnO formation increases in the order:

$$T_{K(OH)} < T_{K(CH_3)} < T_{K(Cl)}.$$

On the basis of results obtained it is clear that substituent in ortho position in benzene ring influences various properties of zinc (II) carboxylates but the influence is not the same.

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STRESZCZENIE

Opracowano warunki preparatyki *o*-metylo-, *o*-hydroksy- i *o*-chlorobenzoesanu cynku (II), zbadano ich skład ilościowy; rozpuszczalność w wodzie w temperaturze 303 K oraz zarejestrowano widma IR i X. R-benzoesany otrzymano jako związki krystaliczne o stosunku molowym metal: ligand organiczny 1:2. Ich rozpuszczalność jest rzędu 10^{-4} – 10^{-6} mol·dm³. Zbadano warunki i produkty rozkładu termicznego kompleksów ogrzewanych w atmosferze powietrza. Kompleksy ogrzewane rozkładają się dwu- lub trój etapowo do ZnO (993–1058 K).

