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Preparation of Non-Valence Compounds of Zinc(II) with 1,2- and 1,4-Benzenedicarboxylic Acids via Self-Assembly

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Abstract—Nanostructured non-valence compounds based on coordination compounds of zinc(II) with phthalic and terephthalic acids have been prepared. The purity and composition of prepared compounds have been elucidated from X-ray diffraction analysis, IR spectroscopy, elemental analysis, and thermogravimetry studies; thermal decomposition of the non-valence compounds has been studied as well. The prepared self-assembled compounds are co-precipitated with one water molecule and 1.5 acetic acid molecules per unit of the dicarboxylic acid: $[Zn_4(OH)_6 \cdot o\text{-}C_6H_4(COO)_2]\cdot H_2O\cdot 1.5CH_3COOH$ and $[Zn_4(OH)_6 \cdot p\text{-}C_6H_4(COO)_2]\cdot H_2O\cdot 1.5CH_3COOH$.

Keywords: non-valence compound, self-assembly, self-organization, guest–host, inclusion compound

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Previously we reported on preparation of inclusion compounds via interaction of formic acid with copper(II) and cadmium(II) complex terephthalates synthesized in slightly acidic medium [1], interaction of cadmium(II) and nickel(II) complex terephthalates with acetic acid [2], and interaction of acetic acid with cadmium(II), cobalt(II), and nickel(II) terephthalates synthesized at pH > 8.5 [3]. Independently of the initial composition, complexes of Cd(II) or Ni(II) with phthalic or terephthalic acid are dehydrated upon the self-assembly and include 0.75 molecules of *guest* acetic acid per the dicarboxylic acid molecule.

The recently emerged interest to various metal phthalates and terephthalates is due to their peculiar layered structure leading in turn to a number of applications as molecular sieves and adsorbents. In particular, copper terephthalate is used for adsorption of N_2, Ar, and Xe [4]. Zinc, calcium, and tin terephthalates are used as promoters of vulcanization in rubber industry, lubricating agents to prevent rubber adhesion to the rollers [5], and capacitive dielectrics [6]; ruthenium terephthalate is a semiconductor [7, 8].

Here we report on preparation of non-valence inclusion compounds based on zinc(II) phthalate or terephthalate synthesized in alkaline medium, and studies of structure and physico-chemical properties of the products. Formic or acetic acid acted as *guests*.

X-ray diffraction patterns of the compounds prepared in the presence of formic acid solutions were identical to those of the initial complex compounds, whereas the diffraction patterns of the compounds prepared in the presence of acetic acid were different. Evidently, the non-valence compounds were formed only in the case of acetic acid *guest* molecules.

Indexing of the diffraction patterns of initial complex zinc terephthalate and the compound prepared via its dissolution in aqueous acetic acid gave the unit cell parameters: 25.84, 16.56, and 14.29 Å (initial complex) and 28.014, 14.72, and 12.64 Å (the non-valence compound). The observed changes of the unit cell parameters confirmed the formation of the *host–guest* compound via self-assembly upon dissolution of the complex in acetic acid solution.

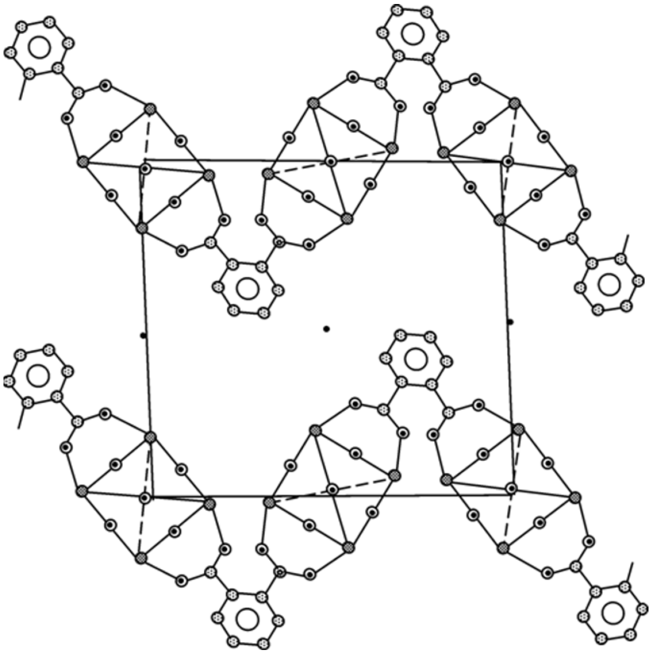
The compounds isolated from acetic acid solutions were studied by means of IR spectroscopy, elemental analysis (Table 1), and TGA (Figs. 2 and 3; Table 2).

Table 1. Elemental analysis results

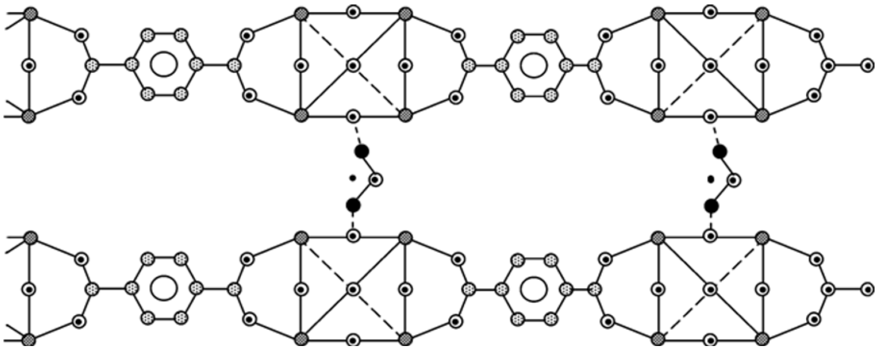
Dicarboxylic acid	Found, %			Formula	Calculated, %		
	H	C	Zn		Zn	C	H
Phthalate	2.93	20.81	41.17	$Zn_4C_{11}H_{18}O_{14}$	41.15	20.77	2.83
Terephthalate	3.01	20.88	41.25	$Zn_4C_{11}H_{18}O_{14}$	41.15	20.77	2.83

IR spectra of the inclusion compounds were very similar to those of the corresponding complexes, the differences being assigned to vibrations of acetic acid carboxy groups: 1728 cm^{-1} (ν_{as}), as well as 1392 or 1350 cm^{-1} (ν_s); as those absorption bands were typical of the free acetic acid, no coordination of the *guest* molecules with the central atoms was revealed [9, 10]. Hence, the coordination properties of phthalate and terephthalate dianions were not changed upon the self-assembly, and the structural unit of the complex compounds remained the same.

In particular, structural units of the complex compounds are zigzag or linear polymeric chains of the $\{Zn_4(OH)_6 \cdot o\text{-}C_6H_4(COO)_2\}_n$ and $\{Zn_4(OH)_6 \cdot p\text{-}C_6H_4(COO)_2\}_n$ composition (Fig. 1). Crystal hydrate



$\{Zn_4(OH)_6 \cdot o\text{-}C_6H_4(COO)_2\}_n$



$\{Zn_4(OH)_6 \cdot p\text{-}C_6H_4(COO)_2\}_n$

Fig. 1. Structural units of the complex compounds.

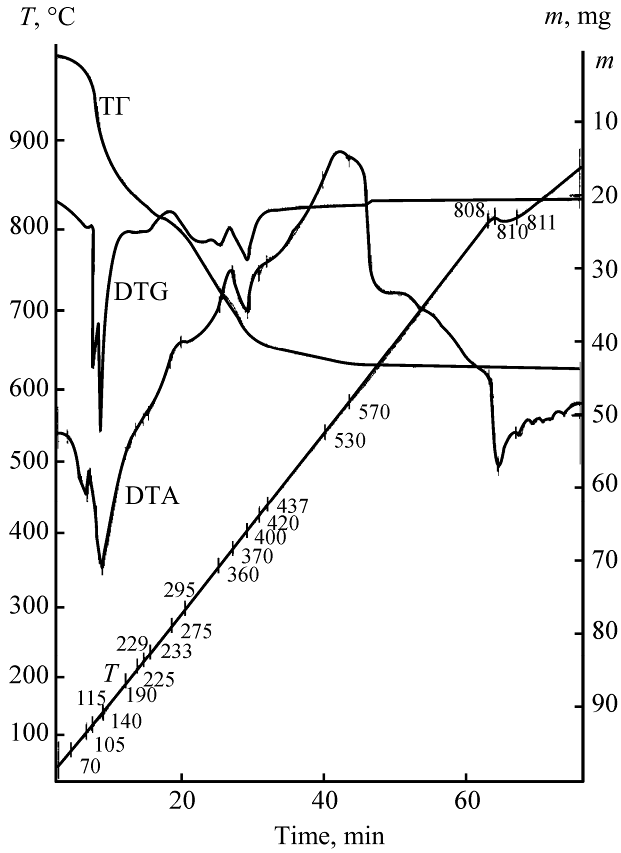


Fig. 2. TGA and DSC curves of $[Zn_4(OH)_6 \cdot o\text{-}C_6H_4(COO)_2] \cdot H_2O \cdot 1.5CH_3COOH$.

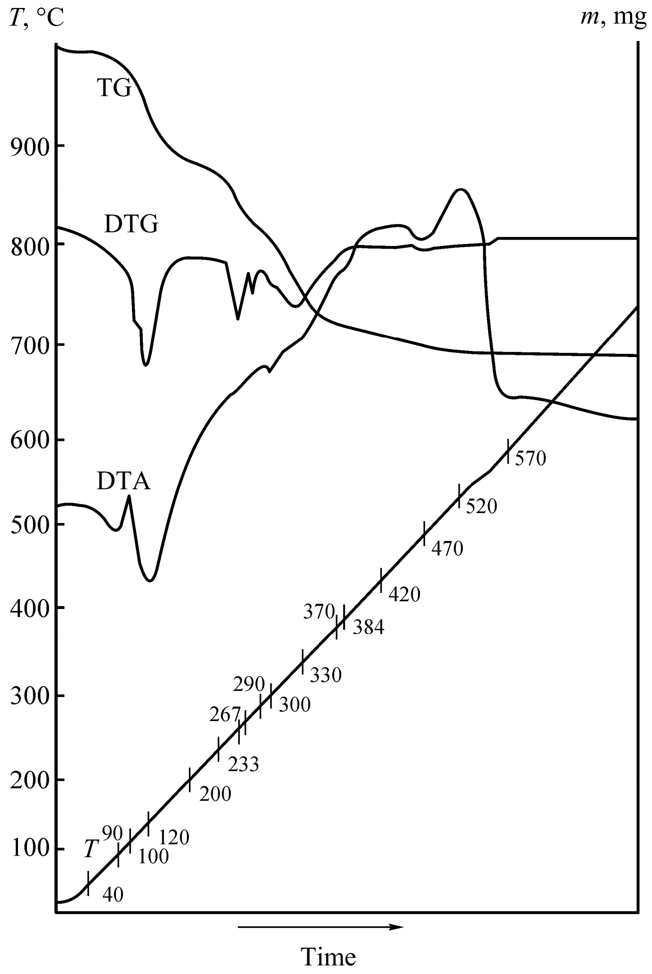


Fig. 3. TGA and DSC curves of $[Zn_4(OH)_6 \cdot p\text{-}C_6H_4(COO)_2] \cdot H_2O \cdot 1.5CH_3COOH$.

water molecules are not coordinated and act as bridges between the polymeric chains.

TGA and DSC traces of the inclusion compounds are presented in Fig. 2. Onset of decomposition of the $[Zn_4(OH)_6 \cdot o\text{-}C_6H_4(COO)_2] \cdot H_2O \cdot 1.5CH_3COOH$ inclusion compound was observed at 70°C and was accompanied with weak but clearly distinguished endothermic effect with the maximum at 105°C corresponding to elimination of one water molecule per a formula unit: the experimentally detected weight loss was 2.4% (calculated 2.8%). Further heating led to rapid elimination of 1.5 molecules of acetic acid at 115–225°C, accompanied with strong endothermic effect (maximum at 140°C); the observed weight loss was 13.6% (calculated 13.16%). Elimination of the *guest* molecule was followed by decomposition of the *host* part of the compound, $[Zn_4(OH)_6 \cdot p\text{-}C_6H_4(COO)_2]$, at 190–275°C. The weight loss at that stage corresponded to elimination of three molecules of the bound water (the observed weight loss 7.2%, calculated 8.5%); the process was accompanied by thermal effects with maxima at 233°C (endo) and 295°C (exo). Further, decomposition of the $Zn_4O_3 \cdot o\text{-}C_6H_4(COO)_2$ intermediate occurred at 295–810°C accompanied by thermal effects with maxima at 370°C (exo), 400°C (endo), and 530°C (exo). The complex shape of the TGA curve evidenced the formation and decomposition of numerous intermediate compounds upon heating. Probably, some catalytic processes are involved, ZnO acting as catalyst. The high-temperature residue is ZnO (weight loss upon burning out of the organic part 20%, calculated 16%; the residual weight of ZnO 56.8%, calculated 51.22%). Additional endothermic process was observed at 808–811°C (maximum at 810°C, no weight loss). It could likely be

Table 2. Quantitative features of thermal decomposition of the studied inclusion compounds

Compound, eliminated species	T_{endo}, °C	$T_{endo, max}$, °C	T_{exo}, °C	$T_{exo, max}$, °C	Weight loss, %	
					found	calculated
$[Zn_4(OH)_6{\cdot}o\text{-}C_6H_4(COO)_2]{\cdot}H_2O{\cdot}1.5CH_3COOH$						
H_2O	70–115	105			2.40	2.80
$1.5CH_3COOH$	115–190	140			13.6	14.16
H_2O (6OH)	225–275	225; 233			7.2	8.5
Phthalate			295–370	300		
	370–420	400				
			420–808	530; 570		
	808–811	810			20.00	16.00
ZnO					56.8	51.22
$[Zn_4(OH)_6{\cdot}p\text{-}C_6H_4(COO)_2]{\cdot}H_2O{\cdot}1.5CH_3COOH$						
H_2O	40–100	90			2.45	2.80
$1.5CH_3COOH$	100–200	110			13.48	14.16
H_2O (6OH)	233–290	267	200–570	384; 420	7.4	8.5
Terephthalate	290–330					
	400–520	470				
			470–570	520	19.5	16.0
ZnO					56.5	51.22

assigned to ZnO transition into another high-temperature modification.

Thermal decomposition of the $[Zn_4(OH)_6{\cdot}p\text{-}C_6H_4(COO)_2]{\cdot}H_2O{\cdot}1.5CH_3COOH$ inclusion compound occurred similarly (Fig. 3). The decomposition started at 40°C and was accompanied with a weak endothermic effect (maximum at 90°C); the observed weight loss of 2.45% was assigned to elimination of one water molecule per a formula unit (calculated 2.80%). Further, the $[Zn_4(OH)_6{\cdot}p\text{-}C_6H_4(COO)_2]{\cdot}1.5CH_3COOH$ intermediate compound decomposition occurred at 100–200°C (maximum of the endothermic effect at 110°C), accompanied with elimination of 1.5 *guest* molecules of acetic acid (the observed weight loss 13.48%, calculated 14.16%).

After elimination of 1.5 acetic acid molecules, the endothermic effect was followed by the exothermic one, and it was prevailing up to the end of the decomposition. However, at 233–290°C a weak endothermic effect was observed (maximum at 267°C), assigned to elimination of three water molecules formed via dehydration of six bridging hydroxy groups of the $Zn_4(OH)_6{\cdot}p\text{-}C_6H_4(COO)_2$ intermediate; the corresponding weight loss was 7.2% (calculated 8.5%). Decomposition of the above-mentioned intermediate started at 290–330°C and was accompanied by a weak endothermic effect with the maximum at 300°C.

Further endothermic effects were observed above 370°C (maximums at 384, 420, and 520°C), where various organic species were formed and burned out. The weight loss at this stage was of 19.5% and corresponded to burning out of the terephthalate part, one of the carboxylic oxygen excluded (calculated 16%); hence, the C–O bond of one of the carboxylic groups was broken. The final decomposition product was ZnO: the observed residal weight 56.5% (calculated 51.22%). The thermal decomposition stages are summarized in Scheme 1.

To conclude, the two studied complex compounds $Zn_4(OH)_6{\cdot}o\text{-}C_6H_4(COO)_2{\cdot}1.5H_2O$ and $Zn_4(OH)_6{\cdot}p\text{-}C_6H_4(COO)_2{\cdot}2H_2O$ were not substantially changed upon the self-assembly with acetic acid, and the

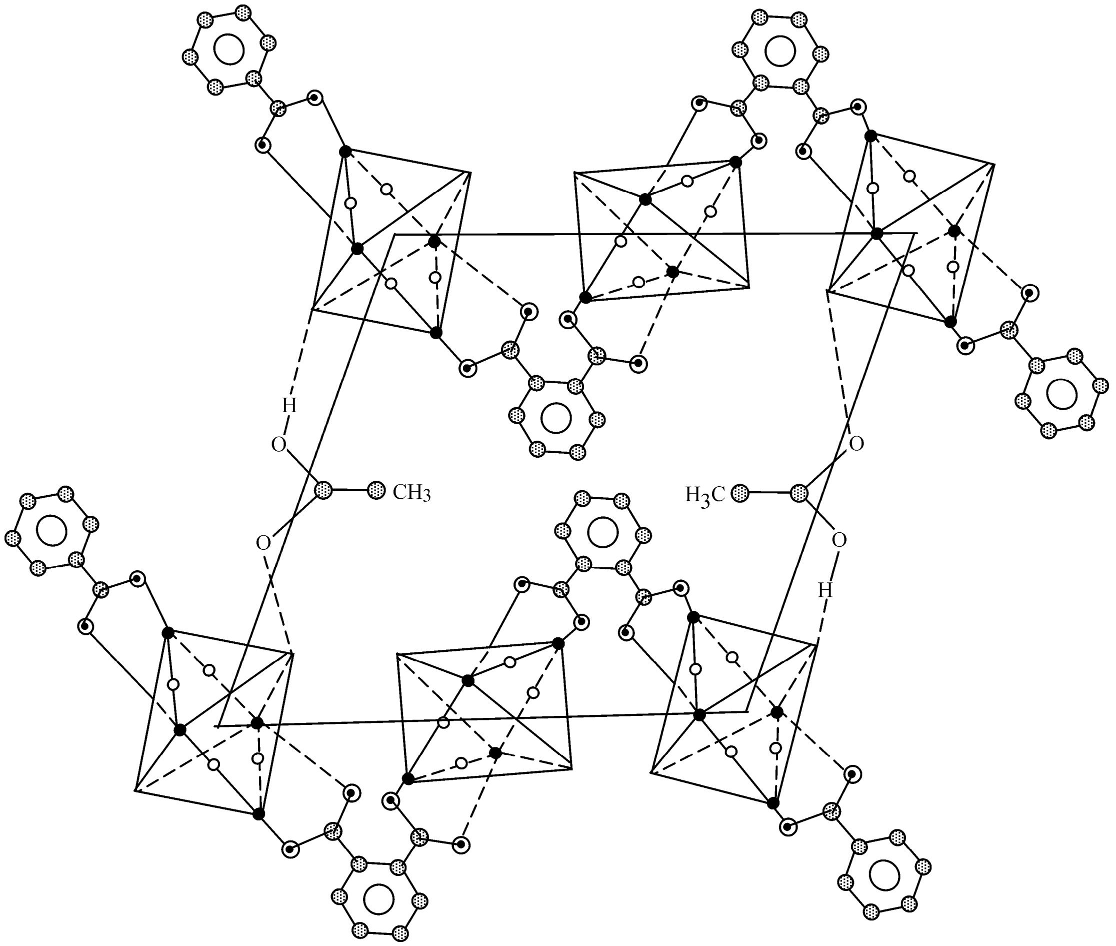


Fig. 4. Possible structure of $[Zn_4(OH)_6{\cdot}o\text{-}C_6H_4(COO)_2]{\cdot}H_2O{\cdot}1.5CH_3COOH$.

structural units of initial complexes were preserved in the inclusion compounds. Formula units of the so formed inclusion compounds were the same in the case of both initial complexes: $[Zn_4(OH)_6{\cdot}o\text{-}C_6H_4(COO)_2]{\cdot}H_2O{\cdot}1.5CH_3COOH$ and $[Zn_4(OH)_6{\cdot}p\text{-}C_6H_4(COO)_2]{\cdot}H_2O{\cdot}1.5CH_3COOH$.

Scheme 1.

$$[Zn_4(OH)_6{\cdot}o\text{-}C_6H_4(COO)_2]{\cdot}H_2O{\cdot}1.5CH_3COOH \xrightarrow[-H_2O]{70\text{–}115\ (105^\circ C)} [Zn_4(OH)_6{\cdot}o\text{-}C_6H_4(COO)_2]{\cdot}1.5CH_3COOH$$

$$\xrightarrow[-1.5CH_3COOH]{115\text{–}190\ (140^\circ C)} Zn_4(OH)_6{\cdot}o\text{-}C_6H_4 \xrightarrow[-3H_2O]{225\text{–}275\ (225,\ 233^\circ C)} Zn_4O_3{\cdot}o\text{-}C_6H_4(COO)_2 \xrightarrow[-o\text{-}C_6H_4(COO)_2]{295\text{–}808\ (300,\ 400,\ 530,\ 570^\circ C)} 4ZnO,$$

$$[Zn_4(OH)_6{\cdot}p\text{-}C_6H_4(COO)_2]{\cdot}H_2O{\cdot}1.5CH_3COOH \xrightarrow[-H_2O]{40\text{–}100\ (90^\circ C)} [Zn_4(OH)_6{\cdot}p\text{-}C_6H_4(COO)_2]{\cdot}1.5CH_3COOH$$

$$\xrightarrow[-1.5CH_3COOH]{100\text{–}200\ (110^\circ C)} Zn_4(OH)_6{\cdot}p\text{-}C_6H_4(COO)_2 \xrightarrow[-3H_2O]{233\text{–}290\ (267^\circ C)} Zn_4O_3{\cdot}n\text{-}C_6H_4(COO)_2 \xrightarrow[-p\text{-}C_6H_4(COO)_2]{290\text{–}570\ (384,\ 420,\ 470,\ 520^\circ C)} 4ZnO.$$

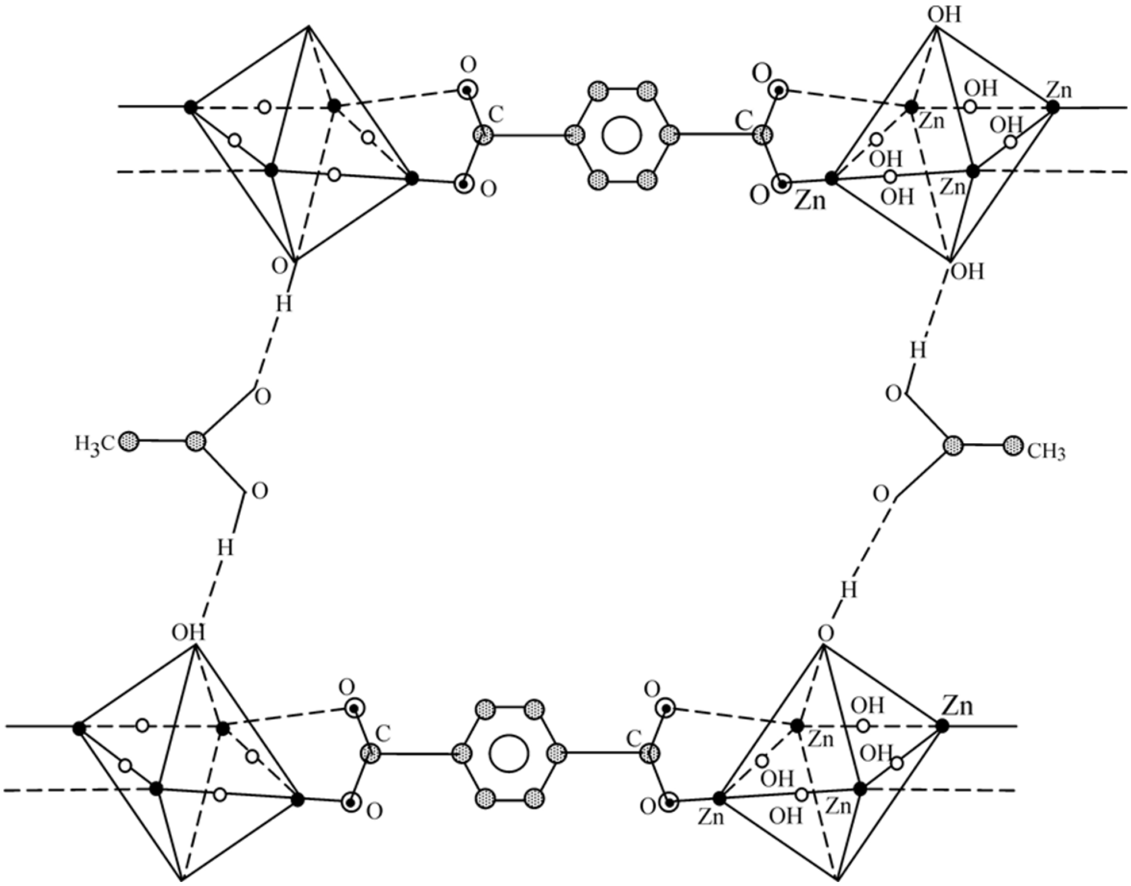


Fig. 5. Possible structure of $[Zn_4(OH)_6 \cdot p\text{-}C_6H_4(COO)_2] \cdot H_2O \cdot 1.5CH_3COOH$.

Basic quantitative features of thermal decomposition of the inclusion compounds are collected in Table 2.

The possible structures of the inclusion compounds are shown in Figs. 4 and 5.

The phthalic acid complex $[Zn_4(OH)_6 \cdot o\text{-}C_6H_4(COO)_2] \cdot H_2O \cdot 1.5CH_3COOH$ (Fig. 4) consists of the tetranuclear metal blocks connected via the bridging OH groups. The tertanuclear blocks are in fact octahedrons with four zinc atoms laying in the same plane, and the bridging hydroxy groups in the octahedron vertexes. The octahedrons are connected via the bridging phthalate dianions. Hence, the virtually infinite zigzag polymeric chains are formed, connected via the hydrogen bonds with guest acetic acid molecules (the hydrogen bonding occurs via carboxylic groups of acetic acid and hydroxy groups in the octahedrons vertexes. Hydrogen bonding results in the polymeric chains shift relative the neighboring ones; hence the three-dimensional supramolecule is formed. The coordination number of Zn(II) equals 5.

The structure of the other inclusion compound, $[Zn_4(OH)_6 \cdot p\text{-}C_6H_4(COO)_2] \cdot H_2O \cdot 1.5CH_3COOH$ is similar to the above-described one. The difference is that in the case of terephthalate the polymeric chains are linear (Fig. 5).

The structural difference of the two studied inclusion compounds was likely reflected in the temperature of the crystal hydrate water elimination (70 and 40°C) in the course of thermal decomposition.

EXPERIMENTAL

X-ray diffraction studies were performed with the Dron-3 (CuK_α radiation; Ni filter) and the Commander Sample ID (Coupled Two Theta/Theta) WL 1.54060 devices. Elemental analysis was performed by gas chromatography (CHNSO E Carlo ERBA analyzer). The metal content was determined from mass of the oxide residue after heating at 800°C. IR spectra were registered with the SPECORD-M80 instrument (400–4000 cm^{-1}).

TGA curves were recorded with the 1500D Paulik-Paulik-Erdey derivatograph (heating at a rate 10 deg/min, Al_2O_3 reference).

The inclusion compounds. The starting compounds were o-$C_6H_4(COOH)_2$, p-$C_6H_4(COOH)_2$, $ZnSO_4 \cdot 7H_2O$, $NaHCO_3$, HCOOH, and CH_3COOH of "pure" grade. The complexes were prepared via interaction of sodium phthalate (terephthalate) with zinc sulfate in alkaline medium. The white crystalline powder recrystallized from the boiling solution was filtered off, washed several times with distilled water, and dried in a drying cabinet at 30°C. The structure of prepared complexes was confirmed by X-ray diffraction, elemental analysis, TGA, and IR spectroscopy.

Certain amount of the complex compound was then dissolved in aqueous acetic or formic acid at slight heating. The hot solutions were filtered, cooled to ambient temperature, and left for evaporation. After a week, the crystalline powder of the inclusion compound precipitated; it was filtered off, washed with cold water, and dried in a drying cabinet at 30°C.

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