ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 7, pp. 1429–1434. © Pleiades Publishing, Ltd., 2013.
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# Clathration of the Complexes of Dicadmium(II) Dihydroxo Aqua Bisphthalate and Tetranickel(II) Hexahydroxo Bisphthalate

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Received February 13, 2012

**Abstract—**Clathrate compounds based on complexes of cadmium(II) and nickel(II) with phthalic acid were synthesized for the first time. According to X-ray diffraction study, elemental analysis, IR spectroscopy, and derivatography the composition and structure of compounds synthesized were established.

**DOI:** 10.1134/S1070363213070219

Constructing molecular and supramolecular materials containing microscopic pores or channel structure is a complex but extremely fruitful area of research. Such materials may find application in the petrochemical industry, environmental cleaning like the destruction of volatile organic compounds. By this time in the areas mentioned above are widely used silica and aluminosilicates having microporous structure similar to the structure of zeolites, due to their thermal stability and also because of the possibility to resize the frame of template molecules in a synthetic approach. Unfortunately, this method does not allow the creatation of more versatile *host*-compounds due to the too simple nature of the building blocks. These studies [1–5] have shown that a variety of frame structures can be obtained using inorganic coordination polymers. The construction of rigid ligands with divergent, exactly positioned centers of binding provides enormous opportunities for the synthesis of special porous materials. These features have been partially realized in [6–8]. The authors have obtained layered coordination polymers based on benzene-2,3,5,6-tetracarboxylic and benzene 1,3,5-tricarboxylic acids. The whole ensemble is a two-dimensional coordination polymer with a layered structure.

In such structures generally planar deformation can easily occur as a result of violation of the order of layers packing (shift, rotation and displacement with the rotation of individual layers). The structures of these types tend to form clathrates, which in the interlayer spaces may contain neutral organic molecules of various sizes. At the "flips" the general motif of the structure is usually preserved, but there is a movement of the layers relative to each other. Therewith interlayer distances vary depending on the size of implanted molecules.

This work consisted in the preparation and structural and chemical study of clathrates based on the complex compounds of $Cd_2(OH)_2C_4H_6(COO)_2{\cdot}H_2O$ and $Ni_4(OH)_6C_6H_4(COO)_2$. As inclusion molecules acetic and formic acids were chosen. The complexes were obtained by reacting sodium phthalate with appropriate water-soluble metal salts in the alkaline medium. The alkaline medium was obtained by adding sodium carbonate solution of 30% concentration resulting in the change of the pH from 6.7 to 8.5. Hydroxides and carbonates are not formed under these conditions [9]. The solution was heated to boiling, filtered while hot and cooled to room temperature. Upon cooling, fell polycrystalline powders colorless or light-green color, respectively, for complexes of cadmium and nickel. The powders were dried on filter paper at room temperature in an oven at 30°C.

Further, the complexes were dissolved in acetic and formic acids at low heat. Solutions to the hot filtered and allowed to crystallize. In the process of slow

**Table 1.** The data of elemental analysis of clathrates **I–III**.

| Comp. no. | Found, % | | | Formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|
| | C | H | M | | C | H | M |
| **I** | 13.94 | 1.78 | 58.88 | $Cd_4C_9H_{12}O_{12}$ | 14.18 | 1.58 | 59.03 |
| **II** | 20.59 | 2.77 | 46.32 | $Cd_2C_8H_{12}O_9$ | 20.13 | 2.52 | 47.15 |
| **III** | 21.60 | 2.71 | 41.67 | $Ni_4C_{10}H_{14}O_{12}$ | 21.40 | 2.50 | 41.87 |

cooling and evaporation of solutions fell lamellar crystals are colorless and pale-green color for the complexes of cadmium and nickel, respectively. The crystals were washed with distilled water and dried on filter paper at room temperature in an oven at 30°C.

The obtained complexes $Cd_4(OH)_6C_4H_6(COO)_2]$ HCOOH (**I**), $Cd_2(OH)_2C_4H_6(COO)_2{\cdot}3H_2O$ (**II**), $[Ni_4(OH)_6C_4H_6(COO)_2]CH_3COOH$ (**III**) were investigated by XRD analysis, differential thermal (DTA) analysis, and IR spectroscopy.

The elemental composition of the products **I – III** synthesized is presented in Table 1. Radiographs of complexes of Cd(II) and Ni(II) and clathrates on their basis are presented in Figs. 1–2. IR spectra of compounds **I–III** are shown in Figs. 3 and 4.

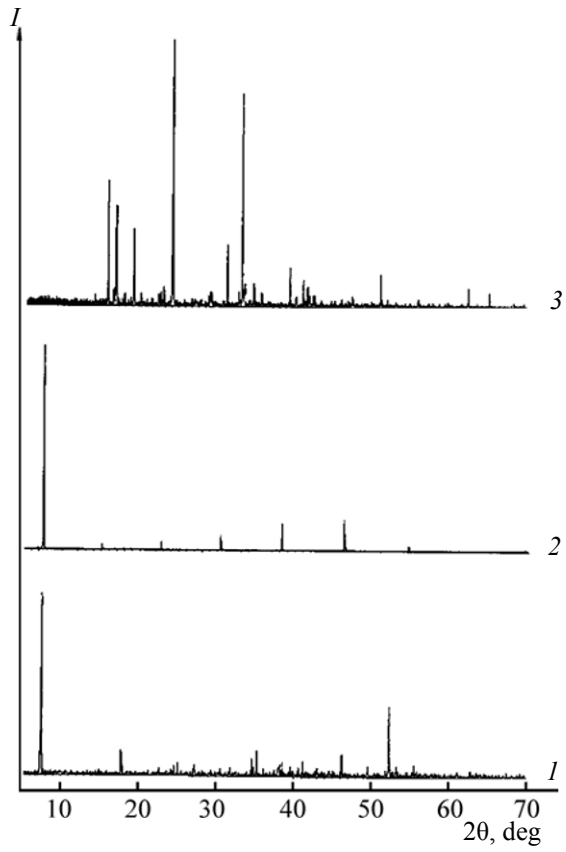


**Fig. 1.** Radiographs of (*1*) $Cd_2(OH)_2C_4H_6(COO)_2{\cdot}H_2O$, (*2*) $Cd_2(OH)_2C_4H_6(COO)_2{\cdot}3H_2O$, and (*3*) $Cd_4(OH)_6C_4H_6{\cdot}(COO)_2]HCOOH$.

Comparison of the IR spectra of complex compound $Cd_2(OH)_2C_4H_6(COO)_2{\cdot}H_2O$ and the clathrate compounds **I** and **II** based on it (Fig. 3) show that in the IR spectrum of the complex compound clear bands at 1420, 1555, and 1585 $cm^{-1}$ are replaced by bands at 1415, 1545, and 1574 $cm^{-1}$ (**I**) and 1450, 1510, and 1540 $cm^{-1}$ (**II**) in the IR spectra of the clathrate compounds. The bands at 1415, 1545, and 1574 $cm^{-1}$ (**I**) and 1450, 1510, and 1540 $cm^{-1}$ (**II**) correspond to the absorption bands of symmetric ($\nu_s$) and asymmetric ($\nu_{as}$) vibrations of the carboxy groups of phthalic acid, which at the clathrate formation are displaced to the areas of higher and lower wave numbers, respectively. The different positions of asymmetric vibrations in the complex and the clathrates show that the carboxy group of phthalic acid has different types of coordination. A the formation of the clathrate and the transformation of the complex

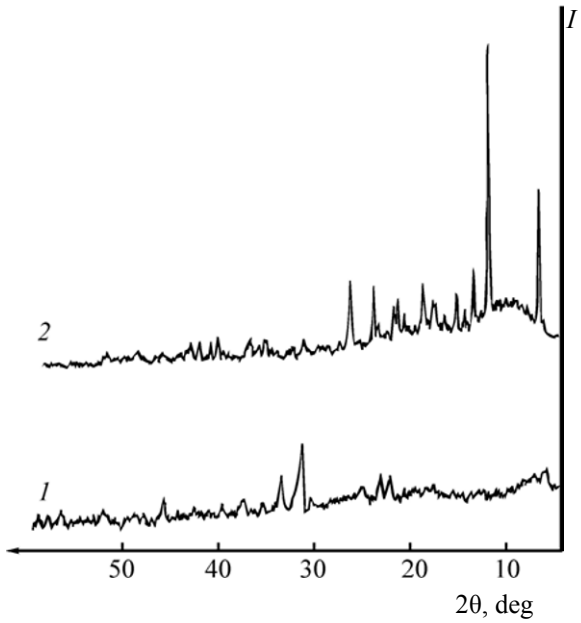


**Fig. 2.** Radiographs of (*1*) $Ni_4(OH)_6C_4H_6(COO)_2$ and (*2*) $[Ni_4(OH)_6C_4H_6(COO)_2]CH_3COOH$.

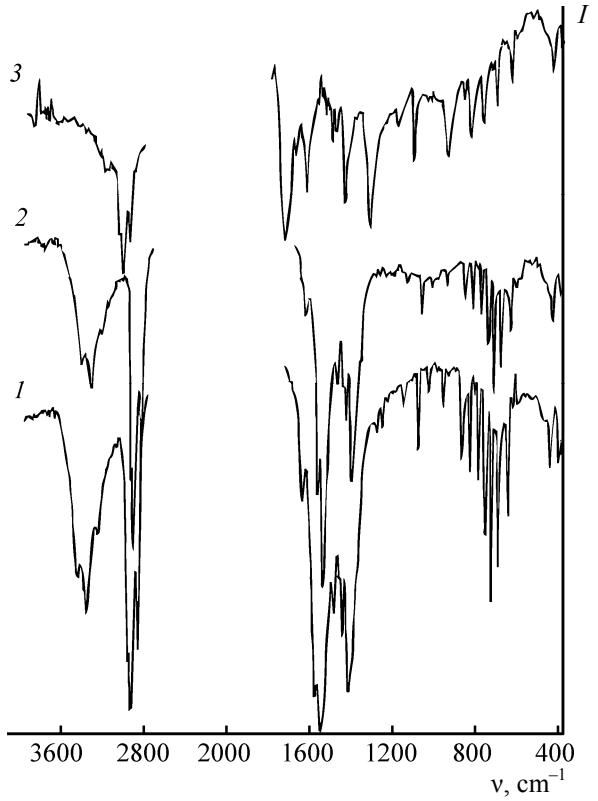


**Fig. 3.** IR spectra of (*1*) $Cd_2(OH)_2C_4H_6(COO)_2{\cdot}H_2O$, (*2*) $Cd_2(OH)_2C_4H_6(COO)_2{\cdot}3H_2O$, and (*3*) $Cd_4(OH)_6C_4H_6{\cdot}(COO)_2]HCOOH$.

into a tetramer the latter includes a molecule of formic acid and in the IR spectrum of the clathrate compound **II** two new bands appear at 1740 and 1325 $cm^{-1}$ (Fig. 3, curve *2*) corresponding to the absorption bands of the asymmetric ($\nu_{as}$) and symmetric ($\nu_s$) vibrations of the uncoordinated carboxy group of formic acid.

As can be seen from Fig. 3, in the IR spectra broad bands are present in the 3700–3100 and 3700–3050 $cm^{-1}$, sharp bands at 3360, 3450 3340, 3426 1647, 1636 $cm^{-1}$, corresponding to the stretching and bending vibrations of OH groups and water molecules [10, 11]. As can be seen from Fig. 3, curve *2* in the IR spectrum of the clathrate compound **II** the broad band in the region 3700–3100 $cm^{-1}$ disappears, but a distinct band at 1640 $cm^{-1}$ remains, attributable to the bending vibrations of OH groups. The bands observed in the IR spectra of the complex and clathrate compounds **I, II** at 965, 1040, 955, 1,025 and 950, 1015 $cm^{-1}$, respectively, belong to the bending vibrations of M–OH bond [10, 11].

The IR spectrum (Fig. 4, curve *1*) of the complex compound $Ni_4(OH)_6C_4H_6(COO)_2$ the asymmetric ($\nu_{as}$)

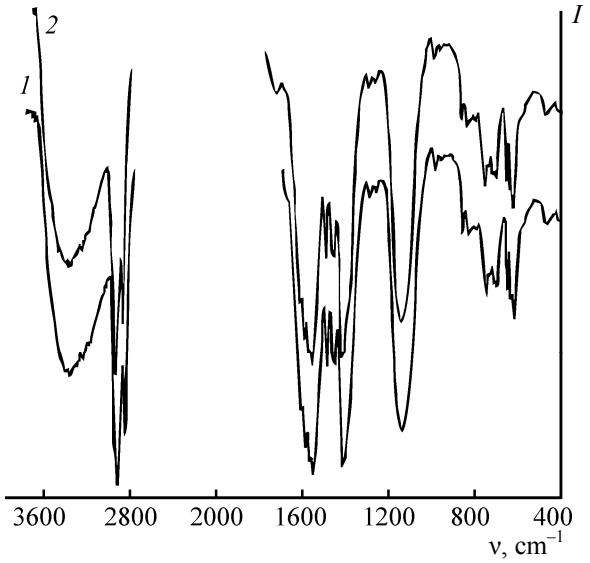


**Fig. 4.** IR spectra of (*1*) $Ni_4(OH)_6C_4H_6(COO)_2$ and (*2*) $[Ni_4(OH)_6C_4H_6(COO)_2]CH_3COOH$.

and symmetric ($\nu_s$) vibrations of the carboxy groups of phthalic acid appear as two distinct bands in the regions 1588, 1555, and 1452 $cm^{-1}$, 1418 $cm^{-1}$ revealing the different form of coordination with the central atom. Also the IR spectrum contains absorption bands at 3700–3016 $cm^{-1}$ and 1610 $cm^{-1}$corresponding to stretching and bending vibrations of OH groups. The bands at 965, 990 $cm^{-1}$, belong to the to bending vibrations of the M–OH bond [10, 11].

The IR spectrum of the clathrate compound **III** (Fig. 4, curve *2*), in contrast to the complex compound, contains new bands at 1730 and 1380 $cm^{-1}$, corresponding to the asymmetric ($\nu_{as}$) and symmetric ($\nu_s$) stretching vibrations of carboxy groups of acetic acid, which clearly indicates that it does not participate in the coordination. In addition, there is only one absorption band at 1595 $cm^{-1}$, characteristic of the asymmetric vibrations of the carboxy groups of phthalic acid at the clathrate formation. This indicates that they are uniformly coordinated to the central atom.

The results of thermal analysis of clathrate compounds are presented in Figs. 5–6 and in Table 2.

As seen from Table 2, in the temperature range of 70–250°C clathrate compound **I** loses 11.6% of its mass, which corresponds to a loss of three water molecules. This is accompanied by an endothermic effect with two peaks at temperatures of 130 and 230°C, i.e., three water molecules from the crystal lattice are removed in two stages. In the first stage 1.5 molecule

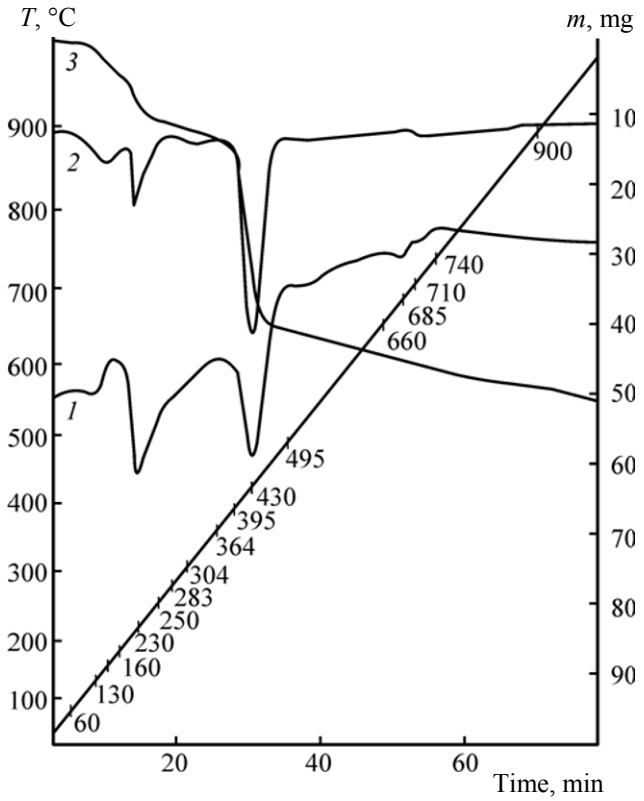


**Fig. 5.** Curves of (*1*) DTA, (*2*) DTG, and (*3*) TG of $Cd_2(OH)_2C_4H_6(COO)_2 \cdot 3H_2O$.

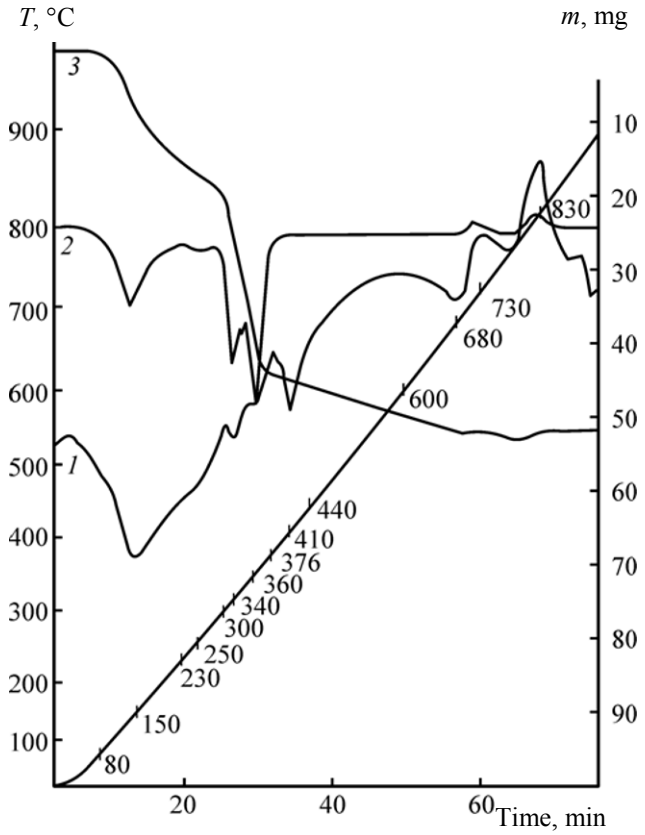


**Fig. 6.** Curves of (*1*) DTA, (*2*) DTG, and (*3*) TG of $[Ni_4(OH)_6C_4H_6(COO)_2]CH_3COOH$.

is lost. The stepwise removal of water molecules is indicated by a shoulder on the TG curve. At higher temperatures on the curve a weak endothermic effect is observed with a maximum at 304°C corresponding to the removal of one molecule of water from two OH groups. In this case the mass loss is 4%. Further, in the temperature range 395–495°C a sharp endothermic effect is recorded with a maximum at 430°C , which

**Table 2.** Results of thermogravimetric studies of compounds **I–III**

| Stage of decomposition | Interval, °C | $T_{max}$, °C | Weight loss, % | |
|---|---|---|---|---|
| | | | found | calculated |
| I – $1.5H_2O$ | 70–180 | 130 | 5.6 | 5.7 |
| – $1.5H_2O$ | 180–250 | 230 | 6.0 | 5.7 |
| – $H_2O$ | 250–364 | 304 | 4.0 | 3.8 |
| – $C_6H_4(COO)_2$ | 395–495 | 430 | 33.6 | 34.4 |
| Complete decomposition | 495–900 | 740 | 50.8 | 54.0 |
| II – HCOOH | 100–200 | 180 | 5.88 | 6.04 |
| – $3H_2O$ | 200–364 | 304 | 6.89 | 7.09 |
| – $C_6H_4(COO)_2$ | 395–495 | 430 | 20.73 | 21.53 |
| Complete decomposition | 495–900 | 740 | 64.24 | 67.44 |
| III – $CH_3COOH$ | 80–230 | 150 | 11.2 | 10.7 |
| – $3H_2O$ | 230–300 | 250 | 9.2 | 9.6 |
| – $C_6H_4(COO)_2$ | 300–376 | 340, 360 | | |
| | 376–440 | 440 | 31.2 | 29.2 |
| Complete decomposition | 470–760 | 600 | 48.8 | 49.6 |
| Oxidation | <760 | 830 | 47.2 | 48.2 |

immediately becomes exothermic in the temperature range 495–900°C with a maximum at 740°C , typical of most phthalates. The mass loss during the endothermic effect was 25.6%, and during the exothermic effect, 8% (Σ 33.6%). The main mass loss in this temperature range is due to the sublimation of the organic residue, and to the exothermic effect caused by combustion of the remainder of the organic residue (up to 900°C). The final thermolysis product is CdO.

Removal of formic acid from the clathrate compound **II** occurs in a single step in the temperature range 100–200°C and is accompanied by an endothermic effect with a maximum at 180°C. In this case the mass loss is 5.88%. In the temperature range 200–364°C in the DTA curve by a very weak endothermic effect is observed with a maximum at 304°C , which corresponds to the removal of three molecules of water from the six OH groups. In this case the mass loss is 6.89%. Further, in the temperature range 395–495°C a sharp endothermic effect is recorded with a maximum of 430°C, which immediately becomes exothermic in the temperature range 495–900°C with a maximum at 740°C, which is characteristic ofor phthalates.

The mass loss that accompanies the endothermic effect is 20.73%. The main mass loss in this temperature range is due to combustion of the remainder of the organic residue (up to 900°C). The final product of thermolysis is also CdO.

In contrast to the clathrate compound **II** the removal of acetic acid from the clathrate compound **III** occurs at a lower temperature (80°C) in a single step accompanied by a broad endothermic effect with a maximum at 150°C and a mass loss of 11.2% weight, which corresponds to the loss of one molecule of acetic acid. The resulting intermediate $Ni_4(OH)_6C_4H_6\cdot(COO)_2$ at 230°C proved to be unstable and decomposed with the loss of three molecules of water from the six OH groups, which is accompanied by a very weak endothermic effect with a maximum at 250°C with weight loss was 9.2%. At higher temperatures 300–376°C two endoeffects were recorded with maxima at 340 and 360°C. The mass loss, accompanying the first endothermic effect is 11.2%, the second endoeffect, 12.8%. This confirms that the carboxy groups are coordinated to the central atom in different ways, that is, they have different types of coordination and therefore the rapture of Me–O occurs at different temperatures. In the temperature range 376–440°C yet another clear endothermic effect is observed with a maximum at 440°C, which is not found in other compounds. As can be seen, the decomposition of intermediate $Ni_4O_3C_6H_4(COO)_2$ occurs stepwise with three accompanying endoeffects and, of course, after each step a rearrangement of the crystal lattice occurs. The process is accompanied by exothermic effect with a maximum at 600°C. The loss of mass at three endothermic and one exothermic effects is 31.2% and is caused by sublimation and the burning of organic residue (up till 760°C). At this temperature, the remaining weight of 48.8% corresponds to a mixture of [Ni+3NiO]. In the X-ray diffractogram of the mixture have the maxima nickel (2.02, 1.742, 1.234, 1.054, 1.010, 0.876, 0.804, 0.783, 0.717) and nickel oxide (2.656, 2,417, 2.303, 2.085, 1,626, 1.476, 1.389, 1.329) [12]. In the TG curve above 760°C an increase in mass occurs with accompanying exothermic effect with a maximum at 830°C. The increase in weight of 1.6% is due to the oxidation of nickel. Thus, the final product of thermal decomposition is NiO.

The original complex compound of cadmium phthalate, despite the fact that is synthesized in an aqueous medium, at the crystallization does not include an additional molecule of water of crystallization. But at the recrystallization in acetic acid, it includes two water molecules, which is apparently due to the fact that on the dissolution in acetic acid the flat part (–COOH) of the acid penetrates into the interlayer channels, expands them and creates the conditions for the penetration of water molecules that form hydrogen bonds with the coordinated water and OH groups and at the same time the lattice parameter perpendicular to the layers increases.

The complex compound $Cd_2(OH)_2C_6H_4(COO)_2\cdot H_2O$ on the dissolution in formic acid includes one molecule of acid to form clathrate compound $[Cd_4(OH)_6C_6H_4(COO)_2]HCOOH$ . As can be seen from the formula at the clathrate formation the complex compound losing one molecule of water is transformed from the dimer in a tetramer. The question arises, why on the dissolution in acetic acid is does not occur? Inability to clathrate formation with acetic acid can be attributed to the sterical shape of $\dot{C}H_3$ group, which makes impossible the full penetration of the acid in the interlayer space, in contrast to formic acid. In the case of formic acid, which is generally flat and easily penetrates the interlayer channels, approaches the coordination sphere, and thence displaces the water

molecule. Therewith the dimeric structure is transformed into tetrameric, formic acid is between the layers and forms a hydrogen bond with the OH groups.

Our studies have shown that on the basis of complex compounds $Cd_2(OH)_2C_6H_4(COO)_2 \cdot H_2O$ and $Ni_4(OH)_6C_6H_4(COO)_2$ it is possible to obtain clathrates that contain the *guest* molecules composed of $H_2O$, $CH_3COOH$, and HCOOH, respectively. The resulting substances have been identified by chemical and physicochemical methods of analysis.

It was established that binyclear structure of the complex compound of cadmium phthalate in forming clathrate with formic acid transforms into a tetramer, which does not occurs at the dissolution of the complex compound in acetic acid. It was also found that the complex when dissolved in acetic acid cannot be include in a molecule of acetic acid due to the sterical factor. Keeping the primary structure, it includes two water molecules.

## EXPERIMENTAL

X-ray powder photographs of compounds (**I-III**) were obtained on diffractometers DRON-3M and D8-ADVANSE ($\lambda Cu K_\alpha$ -radiation, scanning $\theta/2\theta$, $2\theta$ = 60°). Derivatograms were obtained in air on a Q-derivatograph of "MOM" Co (Hungary) coupled with an electronic recording device. Sample weighed 400 mg, the sensitivity was 500 shooting, heating rate 10 deg $min^{-1}$. IR spectra were recorded on the instrument SPECORD-M80 in the range 400–4000 $cm^{-1}$. Elemental composition of obtained compounds was determined by gas-chromotographic method on CHNSO-analyzer "CarloErba". The metal content was determined by the weight loss curve for amount of oxide obtained after heating at derivatograph to 900°C.

**Synthesis of clathrates I–III**. A mixture of sodium salt of phthalic acid and the corresponding water-soluble metal salt and sodium carbonate solution (~30%) was heated to reflux, filtered while hot and cooled to room temperature. Upon cooling poly-crystalline powder precipitated, colorless and light green, respectively, for complexes of cadmium and nickel. Powders were dried on a filter paper at ambient temperature and in a drying cabinet at 30°C. Further complexes were dissolved in acetic or formic acid with gentle heating. Hot solutions were filtered and left for crystallization. During slow cooling and evaporation of the solution formed plate crystals, colorless or light green complexes of cadmium and nickel, respectively. The crystals were washed with distilled water and dried on filter paper at ambient temperature and in a drying cabinet at 30°C.

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