

## STUDY OF THERMAL DEHYDRATION OF $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$

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### ABSTRACT

The dehydration and condensation reactions that take place during calcination of  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  have been followed by means of thermal analyses under non-isothermal (dynamic) and quasi-isothermal–isobaric conditions. Isothermal calcination of starting binary dihydrogenphosphate was carried out in an electric oven at various temperatures and water vapour pressures. The reaction intermediates and products obtained were analysed by instrumental analytical methods and extraction experiments with solutions of water, acetone and 0.3 M HCl. Results have been obtained on the influence of water vapour pressure on the course, rate and yield of the condensation reactions and on the formation of the main product considered here, binary cyclo-tetraphosphate (tetrametaphosphate)  $c\text{-CoMgP}_4\text{O}_{12}$ .

### INTRODUCTION

The cyclo-tetraphosphates can be prepared by thermal dehydration of the dihydrogenphosphates [1] of general formula  $c\text{-Me}_2^{\text{II}}\text{P}_4\text{O}_{12}$  ( $\text{Me}^{\text{II}} = \text{Zn, Mn, Co, Mg, Cd, Ni}$ ). In our laboratory they have been tested as micro-additives to fertilizers with long-term action [2]. Some of them are special thermostable inorganic pigments, and some are luminescent [3,4], anticorrosive [5,6] or coloured [7,8]. Their synthesis has been studied by means of thermal analysis, especially under quasi-isothermal–isobaric conditions [9–12]. Recently we have focused our attention on preparations of binary condensed cyclo-tetraphosphates, i.e. those where one part of the bivalent metal of the (“coloured”) ion is replaced by cheaper ions of alkali earth metals (primarily calcium and magnesium). The cost of the products is decreased and their special properties are improved. These products have not been reported in the literature (no reference to them is made in even the most recent reports) [13–15]. Our latest work has shown the existence of binary condensed phosphates containing magnesium [16,17]. Their general formula is  $\text{Me}_{2-x}^{\text{II}}\text{Mg}_x\text{P}_4\text{O}_{12}$ , where, as a rule,  $x$  can be any value in the whole interval (i.e.  $x \in (0,2)$ ) [18]. The starting raw material is a mixture containing the

bivalent metal concerned and magnesium with a volatile anion and phosphoric acid. The mixture is transformed into the desired product by thermal means [16]. In laboratory experiments designed to determine the basic conditions of the synthesis and to explain the mechanism of dehydration and condensation by which the binary product is formed it is, however, more useful to start with the binary dihydrogenphosphate in a hydrated form, prepared in advance. The present work surveys the results obtained through thermal treatment of  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ .

## EXPERIMENTAL

The starting binary dihydrogenphosphate  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  (blue-violet crystals) was prepared in our laboratory by crystallization of a solution containing  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  ions, concentrated at  $60^\circ\text{C}$ . The quality of the producer was confirmed by atomic absorption spectroscopy and X-ray diffraction analysis, and its morphology by electron microscopy.

In order to elucidate the mass and energy transformations occurring during calcination, the sample was thermoanalysed by the classical dynamic method (i.e. non-isothermal) using a Derivatograph C apparatus (MOM Budapest). The measurements were carried out in a labyrinth crucible under the following conditions; heating rate  $2^\circ\text{C min}^{-1}$ ; sample weight, 155.8 mg; sensitivity of TG, 100 mg; sensitivity of DTA, 6; sensitivity of DTG, 2; and temperature interval,  $20\text{--}500^\circ\text{C}$ . The examination was carried out in the presence of air (Fig. 1).

In order to achieve a better separation of the individual processes occurring during the calcination and to follow the effect of water vapour on their course, we submitted the starting dihydrogenphosphates to TA under quasi-isothermal, quasi-isobaric conditions (Q-TA) [19,20]. The decomposition rate chosen was  $0.3\text{ mg min}^{-1}$  (calculated for a total weight change of 100 mg). The first measurement was carried out under these conditions using the above-mentioned Derivatograph C apparatus, with a crucible with a lid as sample carrier (Fig. 2) (sample weight, 150.65 mg; heating rate,  $1^\circ\text{C min}^{-1}$ ; sensitivity of TG, 50 mg; of DTG, 0.5; of DTA, 2). Further analyses were restricted to thermogravimetric measurements (Q-TG) using the Derivatograph Q-1500 apparatus (MOM Budapest), with four different platinum crucible types as carriers of the sample for thermoanalysis, and a sample weight of about 250 mg (Fig. 3): a multi-plate sample holder (curve A), an open crucible (B), a crucible with a lid (C), and a six-component labyrinth crucible (D). This last arrangement (D) makes it possible to trap the water vapour released during calcination of the starting dihydrogenphosphate, its partial pressure being about 100 kPa (quasi-isobaric conditions) [19,20]. By contrast, in the case of the multi-plate crucible (A), the partial pressure of water vapour in the calcinated sample is so low (about 1 kPa) that in the

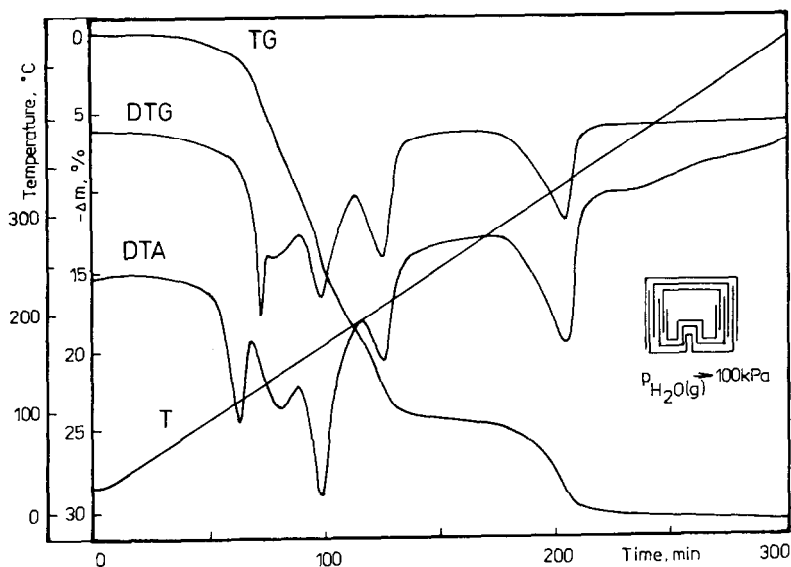


Fig. 1. Simultaneous TG, DTG and DTA curves of  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ , traced under dynamic (non-isothermal) conditions. Apparatus, Derivatograph C; temperature increase,  $0.5^\circ\text{C min}^{-1}$ ; sample weight, 145.8 mg; sensitivity of the balance, TG 50 mg, DTA 2, DTG 2, labyrinth crucible; atmosphere, air.

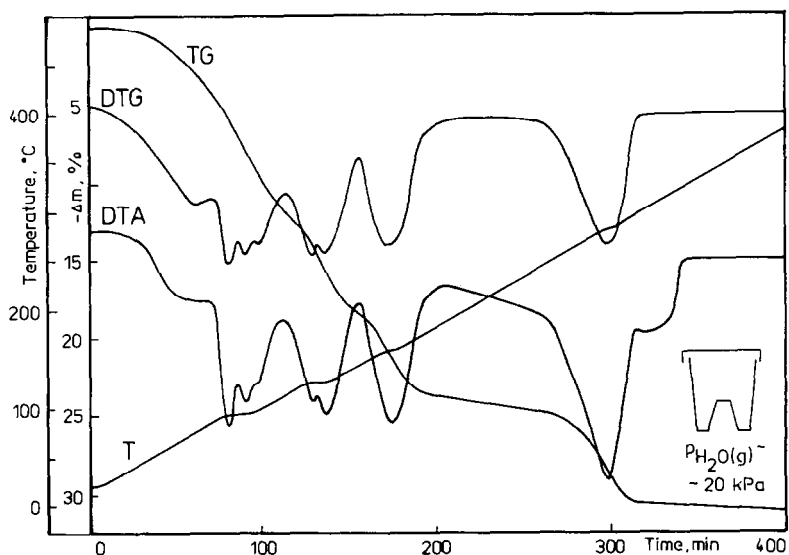


Fig. 2. Simultaneous TG, DTG and DTA curves of  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ , traced under quasi-isothermal, quasi-isobaric conditions: apparatus, derivatograph C; decomposition rate  $0.3 \text{ mg min}^{-1}$ ; temperature increase,  $1^\circ\text{C min}^{-1}$ ; sample weight, 150.65 mg; sensitivity of the balance, TG 50 mg, DTA 2, DTG 0.5; platinum crucible with a lid; atmosphere, air.

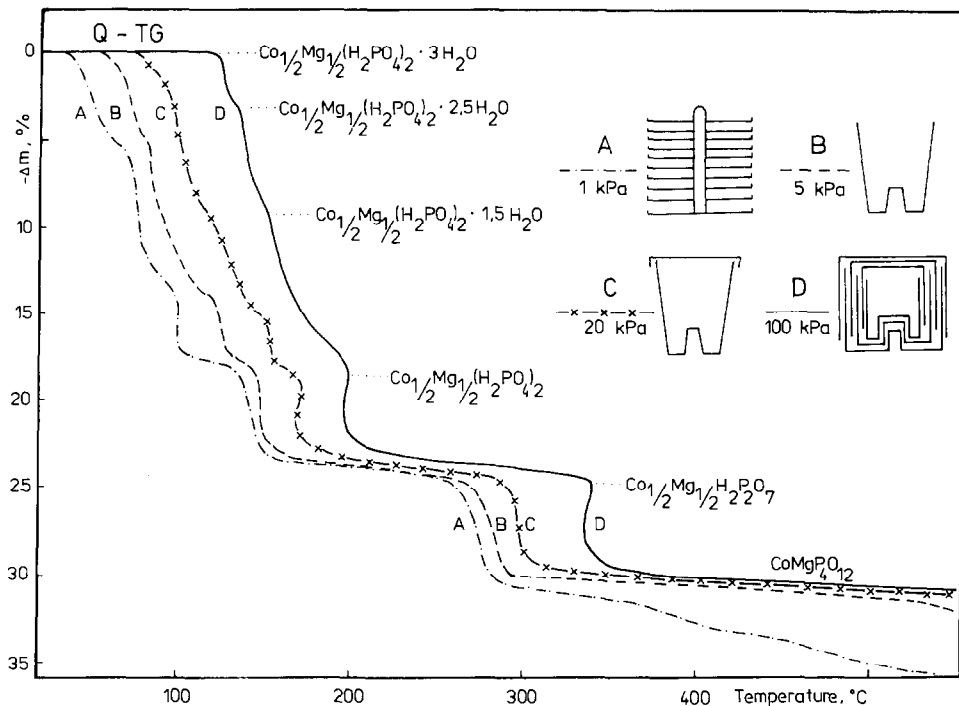


Fig. 3. Thermogravimetric curves of  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  traced under quasi-isothermal, quasi-isobaric conditions: apparatus, derivatograph Q-1500; decomposition rate,  $0.3 \text{ mg min}^{-1}$ ; sample weight, 230 mg; atmosphere, air; (A) multiplate crucible,  $p_{\text{H}_2\text{O}(\text{g})} = 1 \text{ kPa}$ ; (B) open crucible,  $p_{\text{H}_2\text{O}(\text{g})} = 5 \text{ kPa}$ ; (C) crucible with a lid,  $p_{\text{H}_2\text{O}(\text{g})} = 20 \text{ kPa}$ ; (D) labyrinth crucible,  $p_{\text{H}_2\text{O}(\text{g})} = 100 \text{ kPa}$ .

course of the calcination it can be neglected. The corresponding pressure values of crucibles B and C were 5 kPa and 20 kPa respectively [19,20].

The conditions determined from the thermal analysis results were then adopted for the preparation of the main condensation products and intermediates, i.e. the starting dihydrogenphosphates were calcined in an electric oven L 112.2 (VEB Frankhausen, G.D.R.) with a controlled heating rate of  $2^\circ \text{C min}^{-1}$  (Chinotherm 10A, Chinoin Budapest, Hungary) at various temperatures (in the range  $80\text{--}600^\circ \text{C}$ ), each sample being heated for 30 min under isothermal conditions in a flat corundum pan (corresponding to the multi-plate crucible, i.e. 1 kPa water vapour pressure) and in a complex of corundum crucibles (corresponding to the labyrinth crucible, i.e. 100 kPa water vapour pressure).

Following the introductory experiments, the calcinates were extracted using organic solvents (acetone), water and a solution of inorganic compounds (0.3 M HCl) [21,22] (Fig. 4). The extraction experiments allowed investigation of the formation and persistence of various intermediates, especially dihydrogendiphosphate, and the formation of the main product,

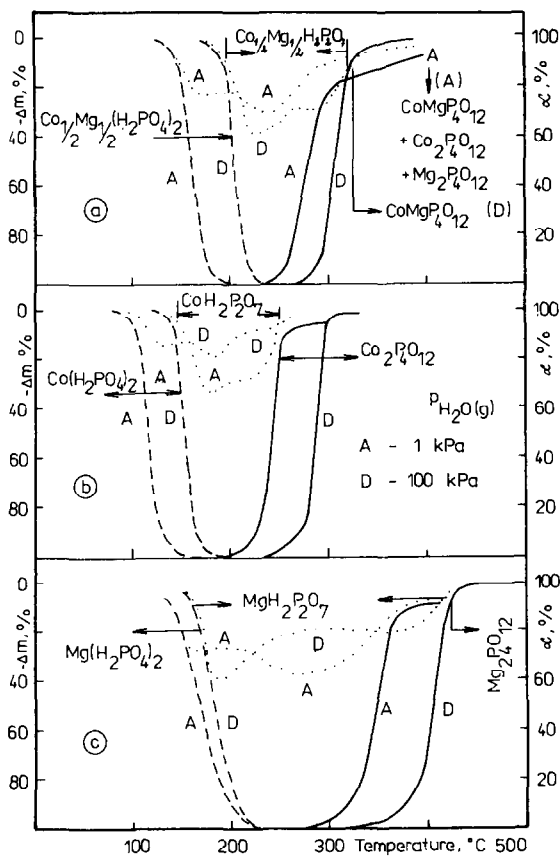


Fig. 4. Extraction experiments on calcinates of the dihydrogenphosphates of Co-Mg (a), cobalt (b) and magnesium (c). Weight changes (calcination conditions,  $p_{\text{H}_2\text{O(g)}}$ : 1 kPa (A), 100 kPa (D)) determined by extraction: acetone (·····); water (---); 0.3 M HCl (—) or degree of conversion ( $\alpha$ ) to the cyclo-tetraphosphates.

cyclo-tetraphosphate. The extraction of the phosphorus component (in the form of phosphoric acid or diphosphoric acid) in acetone can be expressed in terms of the weight decrease after extraction of the calcinate, and as the  $\text{P}_2\text{O}_5$  portion of the total amount in the calcinate. The calcinates were then extracted with water, as the intermediate formed, dihydrogendiphosphate  $\text{Co}_{1/2}\text{Mg}_{1/2}\text{H}_2\text{P}_2\text{O}_7$ , is water soluble. The samples calcined above  $120^\circ\text{C}$  were extracted with 0.3 M HCl, only the final product c- $\text{CoMgP}_4\text{O}_{12}$  (or c- $\text{Co}_2\text{P}_4\text{O}_{12}$  or c- $\text{Mg}_2\text{P}_4\text{O}_{12}$ ) being insoluble. This was done to determine the degree of conversion of  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO})_4 \cdot 3\text{H}_2\text{O}$  into c- $\text{CoMgP}_4\text{O}_{12}$ , c- $\text{Co}_2\text{P}_4\text{O}_{12}$  and c- $\text{Mg}_2\text{P}_4\text{O}_{12}$ , respectively [21].

The starting phosphate and the calcinates were analysed and the individual products prepared by thermal analysis under quasi-isothermal-isobaric conditions identified by thin-layer chromatography [23,24], IR spectroscopy [25] (Perkin-Elmer 684 IR spectrometer), X-ray diffraction analysis [26,27]

(HZG-4 apparatus, G.D.R.), and electron microscopy (Tesla BS 300, C.S.S.R.). The solid residues from each extraction experiment were also analysed by these means. The residues were dissolved by boiling with dilute hydrochloric acid (1 : 1), and the  $\text{Me}^{\text{II}}\text{O}/\text{P}_2\text{O}_5$  ratios determined by atomic absorption spectrometry [28].

## RESULTS AND DISCUSSION

### *TA under dynamic conditions: the labyrinth crucible*

From the thermoanalytic curves (Fig. 1) of the starting Co(II)–Mg(II) dihydrogenphosphate trihydrate (i.e. the binary salt  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ ) recorded under dynamic conditions using the labyrinth crucible (water vapour pressure  $p_{\text{H}_2\text{O}(\text{g})}$  approaching 100 kPa) it is obvious that altogether five endothermic processes take place. These are always connected with mass decreases whose sum is equal to 31.12% of the original sample mass. This decrease is in very close agreement with the theoretical value (31.08%) associated with the release of all five water molecules (three crystal and two constitutional water molecules) from the starting dihydrogenphosphate. One-half molecule of water of crystallization is released during the endothermic process within the temperature interval 100–120 °C (maximum of the endothermic process at 110 °C). The remaining 1 and 1.5 molecules of water of crystallization are released within the temperature intervals 120–155 °C (maximum at 135 °C) and 155–195 °C (maximum at 170 °C) respectively. The two molecules of constitutional water are released during the endothermic processes recorded within the intervals 195–220 °C (maximum at 210 °C) and 290–340 °C (maximum at 330 °C).

### *TA under quasi-isothermal quasi-isobaric conditions*

Figure 2 shows as examples the individual thermoanalytic curves obtained from Q-TA using the crucible with a lid, i.e. with a water vapour pressure of about 20 kPa. It can be seen that the reaction mechanism for release of the three molecules of water of crystallization is more complex at the lower water vapour pressure. The DTA curve shows altogether nine endothermic processes. The first six of these are due to the release of water of crystallization; in the first process, within the interval up to 90 °C, roughly 2/3 molecule of water of crystallization is released, the further 1/2 and 1/3 molecules following at 92 °C and 96 °C respectively. The last three 1/2 molecules of the water of crystallization are released within the temperature intervals 100–110 °C, 110–125 °C and 125–140 °C. The first molecule of constitutional water is released in a single endothermic process within the

interval 140–250 °C, the main part of this (about 4/5) being released within the interval 140–170 °C. The second molecule of constitutional water (usually the fifth molecule is released in an endothermic process which occurs mainly within the interval 250–295 °C. Another less distinct endothermic process, connected with a very small mass change, is observed at temperatures from 295 to 325 °C. This indicates that the second condensation reaction of formation of cyclo-tetraphosphate is partially complicated by side reactions under conditions of lower water vapour pressure.

For these reasons, the TG curves were recorded at quasi-isothermal–isobaric conditions using all four types of crucible as carriers of the sample for thermoanalysis (Fig. 3).

### *Labyrinth crucible*

Curve D (the labyrinth crucible, water vapour pressure approaching 100 kPa) shows breaks corresponding to the release of water of crystallization in two main steps of 1.5 molecules. This is in accordance with the above-mentioned results for dynamic TA using the labyrinth crucible (Fig. 1). The first step is within the temperature interval 120–150 °C and the second is within 150–195 °C. The first section of curve D shows another slight break, which indicates that the first step can be divided into two parts in the intervals 120–135 °C and 135–150 °C, each of which corresponds to the release of one 1/2 molecule of water of crystallization. At 195 °C the calcinate represents the anhydride of binary dihydrogenphosphate,  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2$ . Its presence and binary character were confirmed by instrumental analytical methods (IAM). The overall temperature interval of release of total water of crystallization from  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  (120–195 °C) is shifted 15–20 °C higher as compared with the temperatures of release of water of crystallization, under the same conditions, from the corresponding simple dihydrogenphosphates,  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  (105–180 °C) [9] and  $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  (130–170 °C) [29]. (In a way, this finding confirms that this dehydration phase is not connected with a splitting of the binary dihydrogenphosphate into the simple dihydrogenphosphates.)

The first molecule of constitutional water is released within the temperature interval 200–340 °C, the release of its main part (about three-quarters) being practically isothermal at 200 °C. At the same time the first condensation reaction takes place, producing the intermediate, binary dihydrogendiphosphate  $\text{Co}_{1/2}\text{Mg}_{1/2}\text{H}_2\text{P}_2\text{O}_7$  (also confirmed by IAM). The temperature range of formation and persistence of this important intermediate were also confirmed experimentally: samples of calcinates of the starting  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  (prepared under isothermal conditions in an electric furnace) were extracted with acetone (see Fig. 4, within the interval 200–325 °C). This temperature interval lies roughly between (and partially overlaps) the intervals within which the simple dihydrogendiphosphates  $\text{CoH}_2\text{P}_2\text{O}_7$  and  $\text{MgH}_2\text{P}_2\text{O}_7$  form and persist, as determined by both Q-TA

[9,29] and extraction experiments (Figs. 4b and 4c) (180–240 °C and 170–390 °C for  $\text{CoH}_2\text{P}_2\text{O}_7$  and  $\text{MgH}_2\text{P}_2\text{O}_7$  respectively). Comparison of the three temperature intervals given confirms to a certain extent that the first condensation product formed by calcination of  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  really exists in the binary form  $\text{Co}_{1/2}\text{Mg}_{1/2}\text{H}_2\text{P}_2\text{O}_7$  and not as a mixture of the simple products  $\text{CoH}_2\text{P}_2\text{O}_7$  and  $\text{MgH}_2\text{P}_2\text{O}_7$ . (This result was confirmed by IAM as well as by electron microscopy of both the calcinates and solid residues after acetone extraction.)

The last process consists in the release of the second molecule of constitutional water connected with the second condensation reaction, formation of cyclo-tetraphosphate. In the labyrinth crucible it proceeds within the temperature interval 340–440 °C, the main part (more than three quarters) of this water being released practically isothermally at 340 °C. Above 440 °C the sample mass effectively undergoes no further change, and the product is binary Co(II)–Mg(II) cyclo-tetraphosphate,  $\text{c-CoMgP}_4\text{O}_{12}$  (as confirmed by IAM). This product is a new substance, not yet described in the literature, and is protected by a Czechoslovakian patent [30]. The crystal structure of this product has been determined as a monoclinic system,  $C/2c$  group with structural parameters  $a = 1.1773(5)$  nm,  $b = 0.8285(3)$  nm,  $c = 0.9900(3)$  nm,  $\beta = 118.84(2)^\circ$ ; volume of elementary cell,  $0.8461$  nm<sup>3</sup>; density,  $3.133$  g cm<sup>-3</sup> ( $\rho$  calculated) and  $3.15$  g cm<sup>-3</sup> ( $\rho$  experimental). A comparison of the temperature ranges of formation (under the same conditions) of the respective simple products,  $\text{c-Co}_2\text{P}_4\text{O}_{12}$  and  $\text{c-Mg}_2\text{P}_4\text{O}_{12}$ , shows that they are distinctly different. The cobalt(II) product is formed at lower temperatures (280–295 °C) [9], whereas the magnesium(II) counterpart is formed at higher temperatures (390–460 °C) [29]. These conclusions were confirmed by extraction experiments performed on the calcinates prepared under the appropriate conditions in an electric furnace (0.3 M HCl was used for the extraction: see Fig. 4). At a water vapour pressure of about 100 kPa the calcinations of the individual starting dihydrogenphosphates  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  produce the first portions of the final cyclo-tetraphosphates above temperatures of 250 °C, 350 °C and 280 °C respectively. The final steady state conversion degrees found for the individual calcinates under these conditions were:  $\text{c-Co}_2\text{P}_4\text{O}_{12}$  (at 310 °C), 97%;  $\text{c-CoMgP}_4\text{O}_{12}$  (at 400 °C), almost 98%; and  $\text{c-Mg}_2\text{P}_4\text{O}_{12}$  (at 460 °C), almost 99%.

#### *Multi-plate crucible*

The thermal analysis of  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  under quasi-isothermal–isobaric conditions using the multi-plate crucible (i.e. at a negligible water vapour pressure of 1 kPa in the area of the sample for thermoanalysis) is represented by curve A in Fig. 3. The course of curve A is comparable with that of curve D (the labyrinth crucible) described above. Besides the expected lower temperature values for the individual processes



(usually by 60–80 °C), curve A also exhibits a somewhat different distribution of the water of crystallization portions released in the individual steps. Another difference is a continuous mass decrease of the thermoanalysed sample even after a mass decrease corresponding to the release of five water of crystallization molecules (theoretically 31.08%) has been attained. (Up to the final temperature of Q-TA at 550 °C, this additional mass decrease is 5%.) The calcinates obtained at various temperatures were analysed by IAM, which showed that the mechanism of the dehydration and condensation reactions that occur during calcination of  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  at low water vapour pressure are similar to that for comparable calcinations of simple dihydrogenphosphates of divalent metals [9–12]. However, this mechanism is somewhat different from that we have observed [31] for the calcination of binary calcium(II) dihydrogenphosphates. At low water vapour pressures a part of the phosphorus component is split off from the individual intermediates and products and condenses in independent reactions; however, no extensive splitting of binary intermediates into the simple forms (Co–Mg into cobalt(II) and magnesium(II)) occurs, in contrast with the Co(II)–Ca(II) intermediates in the calcination of  $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  [31].

The first process, corresponding to the release of the first molecule of water of crystallization from the starting  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  in the multi-plate crucible, can be observed (Fig. 3, curve A) in the temperature interval 40–70 °C. The next process, corresponding to the release of 1.25 molecules of water of crystallization, lies within the interval 70–100 °C, the principal part of this release (more than one-half) proceeding almost isothermally at 75 °C. The remaining 3/4 molecule of water of crystallization are released in the interval 100–130 °C, the greater part of this release again taking place isothermally at 100 °C. IAM analyses confirmed that the main intermediate at 130 °C is the anhydride of binary dihydrogenphosphate,  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2$ . Side-intermediates are formed by partial splitting off of phosphoric acid, i.e. mainly  $\text{H}_3\text{PO}_4$  and  $\text{Co}_{1/2}\text{Mg}_{1/2}\text{HPO}_4$ .

Under these conditions, the first molecule of constitutional water is released within the temperature interval 130–250 °C, the greater part of it (more than two-thirds) being liberated practically isothermally at 140 °C. In this case, the main intermediate is the binary dihydrogendiphosphate  $\text{Co}_{1/2}\text{Mg}_{1/2}\text{H}_2\text{P}_2\text{O}_7$ ; the side-intermediates, except the above-mentioned binary hydrogenphosphate ( $\text{Co}_{1/2}\text{Mg}_{1/2}\text{HPO}_4$ ), are the condensation products formed by independent condensation of the separated phosphorus components, among them predominantly the diphosphoric acid  $\text{H}_4\text{P}_2\text{O}_7$ . The formation and persistence of the intermediate  $\text{Co}_{1/2}\text{Mg}_{1/2}\text{H}_2\text{P}_2\text{O}_7$  was confirmed by extraction experiments (Fig. 4) within roughly the same temperature interval of 140–260 °C.

The second molecule of constitutional water is released within the temperature interval 250–300 °C, the predominant reaction being the formation of

the binary Co(II)–Mg(II) cyclo-tetraphosphate,  $c\text{-CoMgP}_4\text{O}_{12}$ . In addition, side-products are gradually formed (particularly at enhanced temperatures), namely, higher polyphosphoric acids and—out of the intermediates of hydrogenphosphate type—the diphosphates  $\text{Co}_2\text{P}_2\text{O}_7$  and  $\text{Mg}_2\text{P}_2\text{O}_7$ . The sample mass decrease above the value corresponding to the release of five water molecules from the starting dihydrogenphosphate is due to the partial volatility of the phosphoric component and to the formation of ultraphosphates. Analysis of calcinates prepared under the same water vapour pressure (1 kPa) in an electric furnace confirmed that  $c\text{-CoMgP}_4\text{O}_{12}$  is the predominant compound in the calcinate up to  $300^\circ\text{C}$ . Its amount in the mixture of final products (at  $500^\circ\text{C}$ ) is more than 60%.

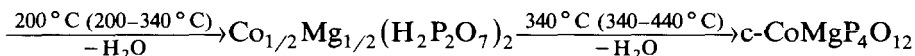
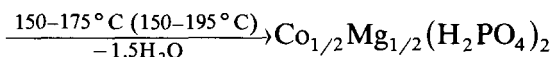
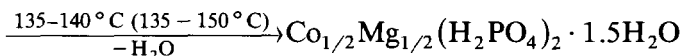
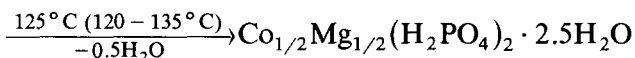
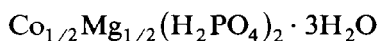
#### *Open crucible and lid-covered crucible*

The TG curves obtained using the open platinum crucible (water vapour pressure, 5 kPa: Fig. 3, curve B) and the lid-covered crucible (water vapour pressure, about 20 kPa: Fig. 3, curve C) are similar in shape to the other two Q-TG curves (Fig. 3, curves A and D) discussed above. Curve B is closer to curve A, whereas curve C is closer to curve D. This means that the mechanism of dehydration and condensation reactions at a  $p_{\text{H}_2\text{O}(\text{g})}$  of about 5 kPa is similar to that described for pressures approaching 1 kPa. (The release of water proceeds gradually over steps corresponding to 1, 1.25, 0.75, 1 and 1 water molecules.) The temperatures of the individual processes are, however, shifted to higher values; these differences are  $10\text{--}25^\circ\text{C}$  and less than  $10^\circ\text{C}$  for the temperatures corresponding to liberation of the water of crystallization and constitutional water molecules respectively. Another difference is obvious from the course of the curve within the temperature interval  $300\text{--}550^\circ\text{C}$ , where the additional mass decrease (above the theoretical value corresponding to five water molecules) is not as distinct as in the case of the multi-plate crucible. This additional mass decrease is only ca. 1%, which means that the undesirable side-reactions of formation of diphosphates, higher polyphosphoric acids and ultraphosphates proceed to a substantially smaller extent; the amount of the main product,  $c\text{-CoMgP}_4\text{O}_{12}$ , in the sample at the end of the analysis is about 80%.

At a water vapour pressure of about 20 kPa (the lid-covered crucible) the mechanism of the calcination reactions of  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  is similar to that described above for a water vapour pressure approaching 100 kPa (i.e. the water release proceeds gradually over steps corresponding to 0.5, 1, 1.5, 1 and 1 water molecules). The temperatures of individual processes are shifted to lower values by  $25\text{--}50^\circ\text{C}$ . Also, the additional mass decrease above  $350^\circ\text{C}$  is only very small (0.3%); hence, the undesirable side-reactions proceed to only a very small extent. After the end of the analysis, the amount of the main product in the sample is about 90%.

## CONCLUSIONS

The course and conditions of the reactions taking place during the calcination of  $\text{Co}_{1/2}\text{Mg}_{1/2}(\text{H}_2\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$  at water vapour pressures in the sample area of around 100 kPa are expressed by the following scheme. (The temperature intervals of the individual processes are given in parentheses and are preceded by the temperature values corresponding to the principal parts of the processes.)



It is possible to prepare the binary cyclo-tetraphosphate  $\text{c-CoMgP}_4\text{O}_{12}$  with yields of almost 98% w/w [32]. This compound has an intensive blue-violet colour which has potential applications (special inorganic pigments for high temperatures [33]).

If the calcination of the starting hydrogenphosphate is performed at lower water vapour pressures, the individual intermediates (anhydride and/or dihydrogenphosphate) are partially split into hydrogenphosphates and phosphoric acid or diphosphates and diphosphoric acid respectively. These substances can then be dehydrated and condensed separately to give side products. The amount of the main product  $\text{c-CoMgP}_4\text{O}_{12}$  in the final calcinate can thus be decreased (even below 60%, at a water vapour pressure approaching 1 kPa). At the same time, the temperatures of most of the individual dehydration reactions are also lowered.

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