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SYNTHESIS AND THERMOSTABILITY OF THE BINARY CONDENSED PHOSPHATES

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Some condensed phosphates, especially cyclo-tetraphosphates have been synthetized as new binary compounds and their existence has been proved. The synthesis of cyclo-$CdMgP_4O_{12}$ is shown as an example. The products crystallize in the monoclinic system (C2c group) and are stable to 900°C. The synthesis is based on a thermal procedure making use of the reversible transformation of cyclo-tetraphosphates to higher linear phosphates (the 1.method) and on a calcination of the starting binary dihydrogenphosphate at quasi-isothermal-isobaric conditions (the 2.method).

Introduction

Binary cadmium(II)-magnesium(II) cyclo-tetraphosphates with cyclic anions have not yet been described in literature. The recent summarizing papers [1-4] giving, inter alia, a number of binary compounds of the condensed phosphate type even allow a conclusion that the existence of these compounds cannot be expected at all [1].

Experimental

The first method [5] suggested by us for preparation of binary cadmium-magnesium cyclo-tetraphosphate [6] is based on a two-step thermal synthesis. The first step starts from pure cyclo-tetraphosphates of the two divalent metals which are melted in normal air atmosphere and then abruptly cooled to give a vitreous amorphous product composed of higher linear phosphates of the summary formula $(CdMg)_{n/4}H_2P_nO_{3n+1}$ [7] . The aliquots of these intermediates are then subjected to DTA (Perkin-Elmer DTA 1700/TADS system) (determination of

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the temperatures T_{Ri} and T_{max} - Fig.1) and are then calcinated in the electric furnace at a temperature by 50°C higher than T_{max}, for 30 min. In this second step the vitreous intermediates recrystallize to the give microcrystalline product c-$CdMgP_4O_{12}$. The yields of the process (α) are determined by the special extraction method [8] . (The same two-step procedure was also applied to the pure c-$Cd_2P_4O_{12}$ and pure c-$Mg_2P_4O_{12}$).

The second method [9] is based on a calcination of the starting binary dihydrogenphosphate $Cd_{1/2}Mg_{1/2}(H_2PO_4)_2 \cdot 3H_2O$ (or mixtures containing phosphorus acid and bivalent metals compounds in the corresponding ratio - $P_2O_5/(Cd+Mg) = 1$). On the basis of our earlier results [10,11] , the dehydration of the starting phosphate was carried out at a higher water vapour pressure in the calcinated sample area (to obtain the maximum conversion degree of the main final product c-$CdMgP_4O_{12}$). For determination of its course, the thermal analyses under quasi-isothermal-isobaric conditions (Fig.2) by means of the Derivatograph Q-1500D (MOM Budapest) and labyrinth crucible as the sample carrier were used. The same conditions were then adopted for the calcination of the starting phosphate in electric furnaces. In order to prove the existence of the intermediates and products, were used the extraction balanced analytical methods developed in our laboratory [8] Fig.3. The results were compared with those published about the corresponding two simple dihydrogenphosphates. The intermediates and final products obtained by both the ways of preparation c-$CdMgP_4O_{12}$ were analyzed by the instrumental analytical methods (chromatography, IR-spectroscopy, X-ray powder diffraction analysis, AAS and electron microscopy). The diffractograms (λ Cu_K = 0.15418 nm) were indexed on the basis of the fact that the binary product c-$CdMgP_4O_{12}$ is isostructural with c-$Cd_2P_4O_{12}$ and c-$Mg_2P_4O_{12}$ [15] .

The products were analyzed from the point of view of thermal stability by the DTA method (DTA-1700 Perkin Elmer) along with high temperature microscopy (MHO-2, Zeiss Jena) to estimate their temperature of melting (Fig.1).

Results and discussion

On the DTA curves the first sections (Fig.1) indicate an exothermic process. This process represents the reaction of formation of the binary tetrametaphosphate from the intermediate of the type of higher linear phosphates (1) which is connected with recrystallization of the amorphous vitreous phase. (The temperatures - T_{Ri}, T_{max} - and heat of this process determined under the conditions of TA are given in Table I).

$$(CdMg)_{n/4}H_2P_nO_{3n+1(glass)} = n/4\,c\text{-}CdMgP_4O_{12(cryst.)} + H_2O_{(g)} \qquad (1)$$

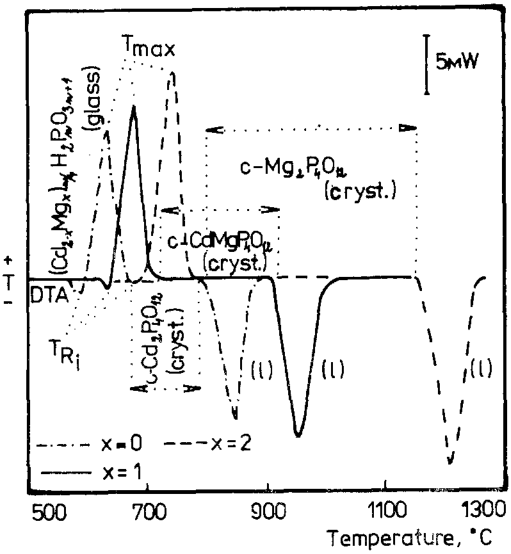

Fig.1

The DTA curves of the vitreous intermediates $(Cd_{2-x}Mg_x)_{n/4}H_2P_nO_{3n+1}$ (x = 0; 1; 2) indicating the formation of the cyclo-tetraphosphate products (by reaction (1)) and their incongruent melting (2).

Temperature increase, 20°C.min^{-1}; sample weight, 15 mg; Pt-crucible (open); atmosphere air.

The analysis of the product prepared in electric furnaces at the temperature of 740°C (T_{max} + 50°C) showed that the yield of this synthesis is high (α = 97.9% - Table I); the molar ratio $P_2O_5/(Cd+Mg)$ determined in the extracted products is equal to 1.0004 and the molar ratio Cd/Mg = 1. The instrumental analytical methods confirmed that each product represents only a single phase, and composition of its anion corresponds to cyclo-tetraphosphate. The structural parameters (a,b,c,V) and density (ρ) of the product lie between the parameters corresponding to the simple cyclo-tetraphosphates of the respective metals (Cd and Mg) - Table I.

As the yield of this synthesis was high, the section of DTA curve above the recrystallization temperature can be considered to determine the thermal stabilities of the binary tetrametaphosphate. The endothermic effects at these DTA curves document their melting - Table I (as it was confirmed by means of high-temperature microscopy) which is incongruent: the tetrametaphosphate are transformed into higher linear phosphates (2), which is favoured by the presence of at least traces of water vapour in the air atmosphere.

$$\text{c-CdMgP}_4\text{O}_{12(\text{cryst.})} + 4/n\text{H}_2\text{O}_{(\text{g})} = 4/n(\text{CdMg})_{n/4}\text{H}_2\text{P}_n\text{O}_{3n+1(\text{l})} \qquad (2)$$

Table I: The conditions of formation c-CdMgP$_4$O$_{12}$, c-Cd$_2$P$_4$O$_{12}$ and c-Mg$_2$P$_4$O$_{12}$ (the 2.method) and their properties

	c-CdMgP$_4$O$_{12}$	c-Cd$_2$P$_4$O$_{12}$	c-Mg$_2$P$_4$O$_{12}$
T_{Ri}/T_{max} (°C)	646/890	596/629	706/745
$-\Delta H$(J.g^{-1})/$\mathcal{L}$(%)	194/97.9	135/87.6	305/99.7
a/b (nm)	1.2004/0.8545	1.2328/0.8639	1.1749/0.8278
c(nm)/V(nm^3)	0.9942/0.8965	1.0388/0.9645	0.9905/0.8433
β°	118.46	119.39	118.92
ρ (g.cm^{-3})calc./exper.	3.353/3.33	3.723/3.85	2,871/2.85
$T_{melt.}$($\sim T_{stab.}$)(°C)	912	800	1160

Cd$_{1/2}$Mg$_{1/2}$(H$_2$PO$_4$)$_2$.3H$_2$O was used as the starting compound for verification of preparation of the requested c-CdMgP$_4$O$_{12}$ by the other technologically easier way. (It was prepared by crystallization from a water solution containg the corresponding molar ratio of Cd^{2+}, Mg^{2+} and phosphate ions by concetrating it at a temperature of 80°C). The thermogravimetric curves obtained under quasi-isothermal-isobaric conditions (labyrinth crucible [15]) are shown in Fig.2.; for comparison also shown are the termogravimetric curves (Q-TG) obtained at the same conditions from the dehydration of samples containing the simple dihydrogenphosphates ($Cd(H_2PO_4)_2.2H_2O$ [13] and $Mg(H_2PO_4)_2.2H_2O$ [14]). Two half molecules of crystal water are released within the temperature interval of 115-165°C under TA of $Cd_{1/2}Mg_{1/2}(H_2PO_4)_2.3H_2O$ conditions in one process. Remaining crystal water is released in the temperature interval of 165-180°C when the binary anhydride $Cd_{1/2}Mg_{1/2}(H_2PO_4)_2$ is formed (the mass decrease is 17.2% the theoretical 17.145% corresponding to the release of three water molecules). The temperatures of formation of the related anhydrides of simple dihydrogenphosphates are 175°C for $Cd(H_2PO_4)_2$ and 170°C for $Mg(H_2PO_4)_2$. The splitting off of the first molecule of constitutional water and the formation of the binary dihydrogendiphosphate $Cd_{1/2}Mg_{1/2}H_2P_2O_7$ conected therewith (first condensation reaction) take place within the temperature interval of 180-310°C; the related simple intermediates,

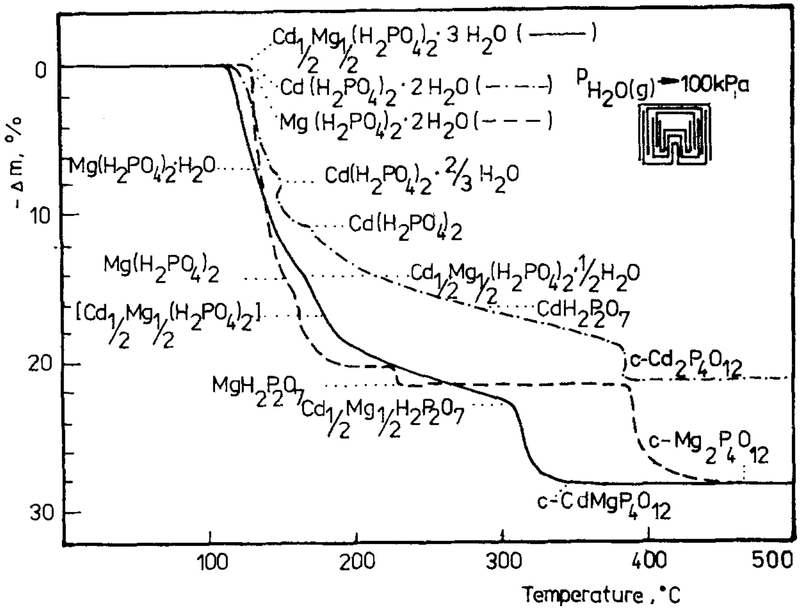

Fig.2 TG curves of starting dihydrogenphosphates under quasi-isothermal, quasi-isobaric conditions. Decomposition rate, 0.2 mg.mm^{-1}; labyrinth crucible,$pH_2O_{(g)}$ = •100 kPa; atmosphere, air.

are formed within the temperature intervals of 175-315°C for $CdH_2P_2O_7$ and 170-230(390)°C for $MgH_2P_2O_7$. The formation of the final binary product, c-$CdMgP_4O_{12}$, connected with the release of the second molecule of constitutional water, and then with the process of the second condensation reaction start within the temperature interval of 310-360°C (the whole mass decrease is 28.65% up to the temperature 340°C and it is not further changed. It is corresponding to the theoretical mass decrease of water of the starting binary dihydrogenphosphate 28.57%). The intervals of formation of the corresponding simple cyclo-tetraphosphates are 315-400°C for c-$Cd_2P_4O_{12}$ and 390-460°C for c-$Mg_2P_4O_{12}$.

The extraction experiments of the samples of starting dihydrogenphosphates prepared in the electric furnace (binary and both simple phosphates) at various temperatures and under conditions corresponding to the TA conditions (the labyrinth crucible and the temperature increase of 2°C.min^{-1}) confirmed the areas of formation and existence of the simple intermediates and final products (along with a good final steady-state conversion degree) Fig.3. The product prepared

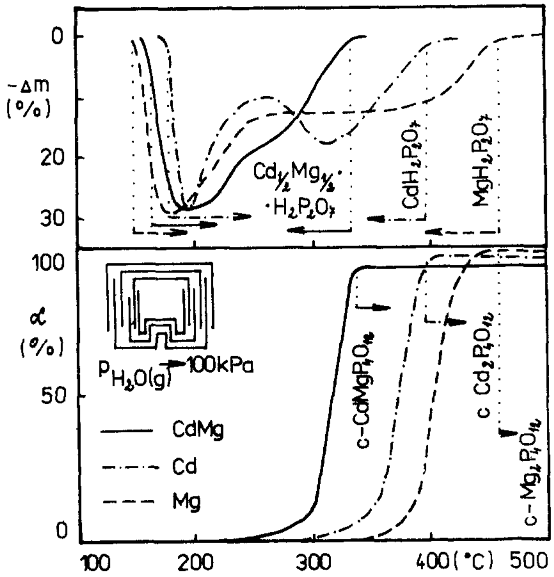

Fig.3

Extraction experiments on Cd-Mg, Cd and Mg intermediates and products. Weight changes (-Δ m) of the intermediates determined by extraction with acetone. Degree of conversion (α) to the cyclo-tetraphosphates (determined by extraction with 0.3M HCl [8] . Calcination conditions, $pH_2O(g)$ = 100 kPa; temperature increase 2°C.min^{-1}; atmosphere air.

at the temperatures above 400°C contained more than 93% c-$Cd_2P_4O_{12}$ [9] . The X-ray diffraction analysis confirmed the crystal structure of product with the parameters corresponding to the values given in Table I also corresponding is the experimentally determined value of density (3.35 $g.cm^{-3}$) and melting temperature (905°C).

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Zusammenfassung - Einige kondensierte Phosphate, im besonderen Zyklotetraphosphate wurden als neue binäre Verbindungen hergestellt. Als Beispiel wird Zyklo-$CdMgP_4O_{12}$ angeführt. Das Produkt kristallisiert monoklin /Gruppe C2/c/ und ist bis 900°C stabil. Die Synthese basiert auf einem thermischen Verfahren unter Anwendung des reversiblen Überganges von Zyklotetraphosphaten zu höhereren linearen Phosphaten /Verfahren 1/ und auf dem Kalzinieren der binären Ausgangsverbindung Dihydrogenphosphat bei quasi-isothermen-isobaren Bedingungen /Verfahren 2/.

Резюме - Осуществлен синтез и доказано наличие некоторых конденсированных фосфатов и в особенности циклотетрафосфатов, как новых двойных соединений. В качестве примера представлен синтез цикло-$CdMgP_4O_{12}$. Полученные соединения кристаллизуются в моноклинной сингонии / группа C2c / и устойчивы до температуры 900°. Первый метод синтеза заключается в термически обратимом превращении циклотетрафосфатов до более высоких линейных фосфатов, а второй метод - в прокаливании исходных двойных дигидрофосфатных солей в квазиизотермических-изобарных условиях .