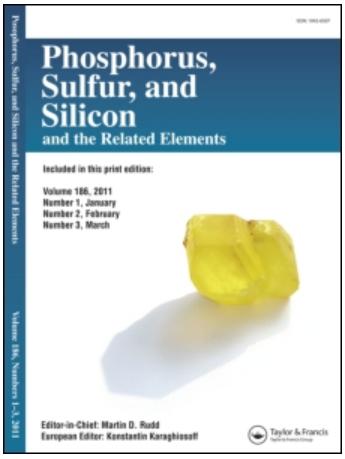

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THE BINARY Cd(II)-Co(II) CYCLO-TETRAPHOSPHATES

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Cadmium (II) – cobalt (II) cyclo-tetraphosphates have been synthesised as new binary compounds. The synthesis is based on a thermal procedure making use of the reversible transformation of cyclo-tetraphosphates to higher linear phosphates. The compounds prepared have been evaluated from the standpoint of their structure, colour hue, density and thermal stability.

Keywords: condensed phosphates; binary cyclo-tetraphosphates; cobalt; cadmium; special pigments; structural parameters; physical properties; thermostability

1. INTRODUCTION

The cyclo-tetraphosphates of some divalent metals have been prepared by the authors and examined for potential applications as special inorganic pigments. It appears economically advantageous to replace a part of the cation (divalent metal) by some cheaper divalent element that could also improve, in some cases, special pigment properties. Such an element, in itself, however, does not give the cyclo-tetraphosphate.

Binary Cd(II)-Co(II) tetraphosphates with cyclic anions have not yet been described in the literature.[1] The recent summarising papers[2–4] giving a number of binary compounds of the condensed phosphate type even allow the conclusion that the existence of these compounds cannot be expected at all.

The aim of this investigation was to obtain the highest possible yields of the cyclo-tetraphosphate, which constitutes the insoluble portion of the calcinate. This would provide possible binding of the problematic cad-

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mium ions that are often present in phosphoric acid, when this is used in the preparation of cyclo-tetraphosphates of bivalent metals serving as special inorganic pigments.[5]

2. EXPERIMENTAL

The procedure for the preparation of $Cd_{2-x}Co_xP_4O_{12}$ is based on a two-step thermal synthesis. The first step starts with the pure cyclo-tetraphosphates of the two divalent metals that are melted in an air atmosphere and then abruptly cooled to give a vitreous product composed of higher linear phosphates $(Cd_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1}$. In the second step this product is repeatedly heated to a suitable temperature and recrystallized to give a microcrystalline product $Cd_{2-x}Co_xP_4O_{12}$.

The starting simple cyclo-tetraphosphates were prepared using the thermal method.[6] In our laboratory this procedure was modified so as to obtain the cyclo-tetraphosphates as pure as possible (see scheme 1, where temperatures in parentheses go for Co products) where M^{II} = Cd (Co).

$$M^{II}CO_3 + 2\,H_3PO_4 \rightarrow M(H_2PO_4)_2 + H_2O + CO_2 \qquad 125\ ^\circ C\ (150\ ^\circ C)$$

$$M(H_2PO_4)_2 \rightarrow MH_2P_2O_7 + H_2O \qquad 215\ ^\circ C\ (180\ ^\circ C)$$

$$MH_2P_2O_7 \rightarrow 1/2\ M_2P_4O_{12} + H_2O \qquad 400\ ^\circ C\ (280\ ^\circ C)$$

SCHEME 1

The synthesis of the binary cyclo-tetraphosphates is described in scheme 2:

$$(1\text{-}x/2)\ Cd_2P_4O_{12}\ (cryst.) + x/2\ Co_2P_4O_{12}\ (cryst.) + 4/n\ H_2O \rightarrow 4/n\ (Cd_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1}(l) \qquad \text{melting}$$

$$4/n\ (Cd_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1}\ (l) \rightarrow 4/n\ (Cd_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1}\ (glass) \qquad \text{solidification}$$

$$4/n\ (Cd_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1}\ (glass) \rightarrow Cd_{2-x}Co_xP_4O_{12}\ (cryst.) + 4/n\ H_2O \qquad \text{recrystallization}$$

SCHEME 2

The values of × were equal to 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0. The mixtures were melted on platinum dishes in an electric furnace by heating to 1100 °C, i.e. above the melting temperature of the higher-melting starting cyclo-tetraphosphate[7,8] ($Co_2P_4O_{12}$, 1060 °C). After 30 min, the dishes with the melts were removed from the furnace and abruptly cooled by immersion in water. The obtained vitreous products $(Cd_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1}$ were dried at 110 °C and ground in a vibrating pebble mill. Other aliquots of these intermediates were then subjected to DTA in order to find the temperatures (T_{Ri}, T_{max}) and heats (ΔH) of the exothermic processes of thermal recrystallization (T_{Ri} is the temperature of the beginning of the reaction of formation $Cd_{2-x}Co_xP_4O_{12}$, T_{max} is the temperature of the maximum of the exothermic effects). The individual intermediates were then calcinated in the electric furnace at temperatures 20 °C higher (T_{max}+ 20°C) for 30 min. The sintered blocks of the individual final products obtained in this way were ground in the vibrating pebble mill. The yields of the process (α) were determined by the special extraction analytical method.[9]

The starting cyclo-tetraphosphates, vitreous amorphous intermediates and final products were analysed by X-ray diffraction analysis. Structural parameters of products were determined by means of X-ray powder diffraction ($Cu_{K\alpha}$ $\lambda = 0.154178$ nm, HZG-4B apparatus Germany). The diffractograms were indexed under the presumption that the mixed cyclo-tetraphosphates are isostuctural with $Cd_2P_4O_{12}$ and $Co_2P_4O_{12}$. The lattice parameters of the monoclinic unit cell (C2c group) were calculated by the least square's method.

The final products were also evaluated by the pycnometric method to estimate their densities and their optical reflectance in the visible region (from 400 to 700 nm) of light.

3. RESULTS AND DISCUSSION

The methods of thermal analysis facilitate detection and explanation of processes that accompany melting of the cyclo-tetraphosphates and their recrystallization. Available papers dealing with their preparation do not give sufficiently precise data on the calcination temperatures necessary for the condensation reactions.

An exothermic process was indicated by means of the DTA method. This process represents the reaction of formation of the binary cyclo-tetraphosphate from intermediate higher linear phosphates that are connected with recrystallization of the amorphous vitreous phase (2). The temperatures (T_{Ri}, T_{max}) and the heats (ΔH) of this process determined by DTA with increasing cobalt content are tabulated in Table I. The yields (α) of this synthesis are high and increase with increasing cobalt content. The molar ratio P_2O_5/(Cd+Co) in the extracted (0.3 M HCl) product varies from 0.9996 to 1.0011, and the molar ratio Cd/Co corresponds very closely to the value's (2-x)/x. Each product represents only a single-phase material and its anion corresponds to cyclo-tetraphosphate. Hence, the products are a type of binary cadmium(II)-cobalt(II) cyclo-tetraphosphates of formula $Cd_{2-x}Co_xP_4O_{12}$. This conclusion applies to the whole range of $\times$ (Table II).

The structural parameters of the products (Table II) a, b, c, angle β and V (the volume of the elementary unit cell) slowly but distinctively decrease with increasing proportion of cobalt. Their values practically lie in the intervals limited by the structural parameters of the pure simple cyclo-tetraphosphates $Cd_2P_4O_{12}$ and $Co_2P_4O_{12}$. Also the volume of the elementary cell of the binary products V quite regularly decreases in the same direction, which is in accordance with the fact that the ionic radius of cobalt ($r[Co^{2+}]$=0.074 nm) is smaller than that of cadmium ($r[Cd^{2+}]$=0.095 nm).

TABLE I The conditions of formation of $Cd_{2-x}Co_xP_4O_{12}$

x	T_{Ri} (°C)	T_{max} (°C)	$-\Delta H$ ($J.g^{-1}$)	yield α (%)
0	592	629	135	87.6
0.25	597	636	134	89.1
0.50	602	640	133	90.6
0.75	608	647	132	92.3
1.00	613	651	132	94.1
1.25	619	656	131	95.8
1.50	625	662	131	96.5
1.75	631	668	130	97.1
2.00	635	673	130	98.2

TABLE II The structural parameters of $Cd_{2-x}Co_xP_4O_{12}$

x	a (nm)	b (nm)	c (nm)	β (deg)	V (nm^3)	$\Delta 2\upsilon^a$
0	1.2328(4)	0.8639(3)	1.0388(3)	119.32(2)	0.9645	0.008
0.25	1.2285(5)	0.8635(4)	1.0335(4)	119.30(2)	0.9561	0.009
0.50	1.2253(4)	0.8627(4)	1.0278(4)	119.24(2)	0.9481	0.011
0.75	1.2132(6)	0.8602(4)	1.0152(6)	118.85(3)	0.9281	0.015
1.00	1.2015(8)	0.8576(4)	0.9882(9)	118.48(5)	0.8951	0.018
1.25	1.1976(8)	0.8539(4)	0.9878(9)	118.45(5)	0.8885	0.018
1.50	1.1945(8)	0.8503(5)	0.9874(9)	118.43(5)	0.8819	0.018
1.75	1.1881(7)	0.8412(6)	0.9882(5)	118.56(5)	0.8641	0.016
2.00	1.1799(5)	0.8304(4)	0.9887(4)	118.70(3)	0.8496	0.013

a. $\Delta 2\upsilon = N^{-1}(2\upsilon_{exp} - 2\upsilon_{calc})$, where $2\upsilon_{exp}$is the experimental diffraction angle, $2\upsilon_{calc}$ is the angle calculated from lattice parameters and N is the number of investigated diffraction lines.

Some physical properties of the products determined with respect to their potential application as special pigments are summarised in Table III. As the yields of this synthesis were high, the sections of DTA curves above the recrystallization temperature can be considered to determine the thermal stabilities of the binary cyclo-tetraphosphates. The endothermic effects on the DTA curves document their melting (as confirmed by means of high-temperature microscopy) which is incongruent. The cyclo-tetraphosphates are transformed into higher linear phosphates, which is favoured by the presence of at least traces of water vapour in the air. Hence, under these conditions the melting temperatures represent the temperatures up to which the binary cyclo-tetraphosphates are stable. They increase with the cobalt content from 800 to 1060 °C. This fact documents the high thermostability of the products that extends the range of their applications to high-temperature purposes.

Also the densities of the binary cadmium(II)-cobalt(II) cyclo-tetraphosphates continuously change with the cobalt content, however; according to expectation, the density values decrease with increasing x, the experimental values ($\rho_{exp.}$) are consistent with the density values calculated ($\rho_{calc.}$) on the basis of the X-ray diffraction analysis.

The colour hue of the binary products is violet. The intensity of the hues decreases with increasing cadmium content in the product. The not very

expressive colour of these products (especially when the content of Cd is high) is advantageous for their application as special anticorrosive pigments of high thermal stability. The coatings containing these anticorrosive pigments may be easily coloured to the desired hue by means of cheaper classical pigments.

TABLE III Melting temperatures and densities of $Cd_{2-x}Co_xP_4O_{12}$

x	$T_{melting}$ (°C)	$\rho_{exp.}$ ($g.cm^{-3}$)	$\rho_{calc.}$ ($g.cm^{-3}$)
0	800	3.85	3.723
0.25	831	3.71	3.692
0.50	865	3.65	3.661
0.75	905	3.62	3.632
1.00	930	3.63	3.601
1.25	963	3.59	3.535
1.50	996	3.53	3.468
1.75	1 032	3.47	3.431
2.00	1 060	3.41	3.391

4. CONCLUSION

The cyclo-tetraphosphates of the type $Cd_{2-x}Co_xP_4O_{12}$, where $\times = 0$, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75 and 2.0, have been synthetised as new binary compounds. The structure of the binary cyclo-tetraphosphates belongs to the monoclinic system, C2c group. The synthesis is based on a thermal procedure making use of the reversible transformation of cyclo-tetraphosphates to higher linear phosphates. This is the method used in our work place for synthesis of special pigments of binary cyclo-tetraphosphates, especially some bivalent metals combined with cobalt.

It is necessary in view of the fact of the possible presence of ecologically undesirable cadmium ions in starting phosphoric acid to know the conditions of probable origin of cadmium (II) – cobalt (II) binary cyclo-tetraphosphates. Phosphoric acid, frequently containing ecologically and hygienically inconvenient cadmium ions, is the starting raw material for

the synthesis of cyclo-tetraphosphates of single bivalent metals (which are base for synthesis of binary cyclo-tetraphosphates). Admission of cadmium ions into the binary phosphate compounds (by high-temperature preparation of above mentioned special pigments may provide a solution for their elimination). Products of the $Cd_{2-x}Co_xP_4O_{12}$type would have remained in this way as chemically and thermally stable (nonsoluble problems in the special pigments).

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