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New Colour Compounds Binary Cyclo-tetraphosphates $Mn_{2-x}Co_xP_4O_{12}$ and $Zn_{2-x}Co_xP_4O_{12}$

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ABSTRACT

The cyclo-tetraphosphates of the type $M^{II}_{2-x}Co_xP_4O_{12}$, in which M^{II} is Mn or Zn and $x \in (0;2)$, have been synthesized as new binary compounds. The coloured products crystallize in the monoclinic system, C2c group. Their structural parameters have the values: (Mn–Co or Zn–Co) a = *1·1799 to 1·2076 or 1·778 nm,* b = *0·8304 to 0·8484 or 0·8305 nm,* c = *0·9887 to 1·0152 or 0·9910 nm,* β = *118·70° to 119·32° or 118·83° and the value of elementary cell* V = *0·8497 to 0·9068 or 0·8492 nm*^{3}.

INTRODUCTION

The cyclo-tetraphosphates of some simple divalent metals have been previously prepared in the authors' laboratories and examined for potential applications as special inorganic pigments.[1] It appeared advantageous to replace a part of the cation by some divalent element which could improve, in some cases, pigment properties such as colour hue and thermal stability. Such a suitable element is, for example, cobalt. The binary manganese(II)–cobalt(II) or zinc(II)–cobalt(II) tetraphosphates with cyclic anions have not been previously described in the literature (cf. Refs 2–5).

EXPERIMENTAL PROCEDURE

The procedure for the preparation of binary manganese(II)–cobalt(II) cyclo-tetraphosphates[6] and zinc(II)–cobalt(II) cyclo-tetraphosphates[7] is based on a

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two-step thermal synthesis. The first step starts from a mixture of pure cyclotetraphosphates 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 general formula $(M^{II}_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1}$.[8] In the second step this product is repeatedly heated to a suitable temperature and recrystallized to give a microcrystalline product $Mn_{2-x}Co_xP_4O_{12}$ or $Zn_{2-x}Co_xP_4O_{12}$.

Preparation of the starting product $Mn_2P_4O_{12}$, $Zn_2P_4O_{12}$ and $Co_2P_4O_{12}$

The starting simple cyclo-tetraphosphates were prepared on the basis of the thermal method described in Ref. 2. This procedure has been modified[9] so as to obtain the products as pure as possible (Scheme 1).

$$M^{II}CO_3 + 2H_3PO_4 \xrightarrow[-H_2O\ -CO_2]{120(170)[180]^\circ C} M(H_2PO_4)_2$$

$$\xrightarrow[-H_2O]{205(260)[240]^\circ C} MH_2P_2O_7 \xrightarrow[-H_2O]{310(325)[295]^\circ C} M_2P_4O_{12}$$

$$M^{II} = \text{Mn(Zn), [Co]; } pH_2O_{(g)} \sim 100\,\text{kPa}$$

Scheme 1

Preparation of $Mn_{2-x}Co_xP_4O_{12}$ and $Zn_{2-x}Co_xP_4O_{12}$

The synthesis of the binary cyclo-tetraphosphates is outlined in Scheme 2.

$$(1-x/2)M^{II}_2P_4O_{12(cryst.)} + x/2Co_2P_4O_{12(cryst.)} + 4/nH_2O$$

$$\xrightarrow[\substack{\text{melting in air}\\ \text{wet atmosphere}}]{1100^\circ C} 4/n(M_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1(l)}$$

$$\xrightarrow[\text{(solidification)}]{1100\rightarrow 25\ C} 4/n(M_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1(glass)}$$

$$\xrightarrow[\text{(recrystallization)}]{T_{R_1}} M^{II}_{2-x}Co_xP_4O_{12(cryst.)} + 4/nH_2O$$

$$M^{II} = \text{Mn, Zn}$$

Scheme 2

The x value in the above was equal to 0·25, 0·50, 0·75, 1·00, 1·25, 1·5 and 1·75. The same two-step procedure was also applied to the pure $Mn_2P_4O_{12}$ and

$Zn_2P_4O_{12}$ ($x = 0$) and pure $Co_2P_4O_{12}$ ($x = 2$). 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 ($Co_2P_4O_{12}$, 1060°C). After 30 min, the dishes were removed from the furnace and abruptly cooled by immersion in water. The vitreous products $(M^{II}_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1}$ were dried at 110°C and ground in a vibrating pebble mill. Other aliquots of these intermediates were then subjected to DTA (DTA 1700 with DSC Mode, Perkin Elmer[10]) in order to determine the temperatures and heats of the exothermic processes of the thermal recrystallization (temperatures T_{Ri}, T_m and ΔH). The individual intermediates were then calcinated in an electric furnace at temperatures 10°C higher ($T_m + 10$°C) for 30 min. The sintered blocks of the individual final products obtained in this way were ground in a vibrating pebble mill. The yields of the process (α) were determined by the previously described special extraction analytical method.[11]

Evaluation of quality of the starting phosphates, products and intermediates

The starting cyclo-tetraphosphates, vitreous amorphous intermediates and final products (binary cyclo-tetraphosphates) were analyzed by TLC,[12] IR,[13] X-ray diffraction[14] and atomic absorption spectrometry.

Structural parameters of the products were determined by means of X-ray powder diffraction ($\lambda Cu_{K\alpha} = 0{\cdot}154\,178$ nm, HZG-4B apparatus FRG).[15] The diffractograms were indexed under the presumption that the binary cyclo-tetraphosphates are isostructural with $Mn_2P_4O_{12}$, $Zn_2P_4O_{12}$ and $Co_2P_4O_{12}$;[16] the lattice parameters of the monoclinical elementary cell (C2c group) were calculated by the squares treatment.

The products were analyzed by the pycnometrical method to estimate their density and by the DTA method (DTA-1700 with DSC Mode, Perkin Elmer,[10] together with high-temperature microscopy (MHO-2, Zeiss Jena) to estimate their temperatures of melting. The reflectance factor of the products in the visible region was measured by means of a Specol 10 apparatus (Zeiss Jena) equipped with the respective 45/0 adapter.

RESULTS AND DISCUSSION

Figure 1 illustrates the DTA curves of the vitreous intermediates $(M^{II}_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1}$ for $x = 0, 0{\cdot}25, 0{\cdot}5, 0{\cdot}75, 1{\cdot}0, 1{\cdot}25, 1{\cdot}5, 1{\cdot}75$ and $2{\cdot}0$. The first sections of the curve indicate an exothermic process. This process represents the reaction of formation of the binary cyclo-tetraphosphates $Mn_{2-x}Co_xP_4O_{12}$ and $Zn_{2-x}Co_xP_4O_{12}$ which is connected with the initial

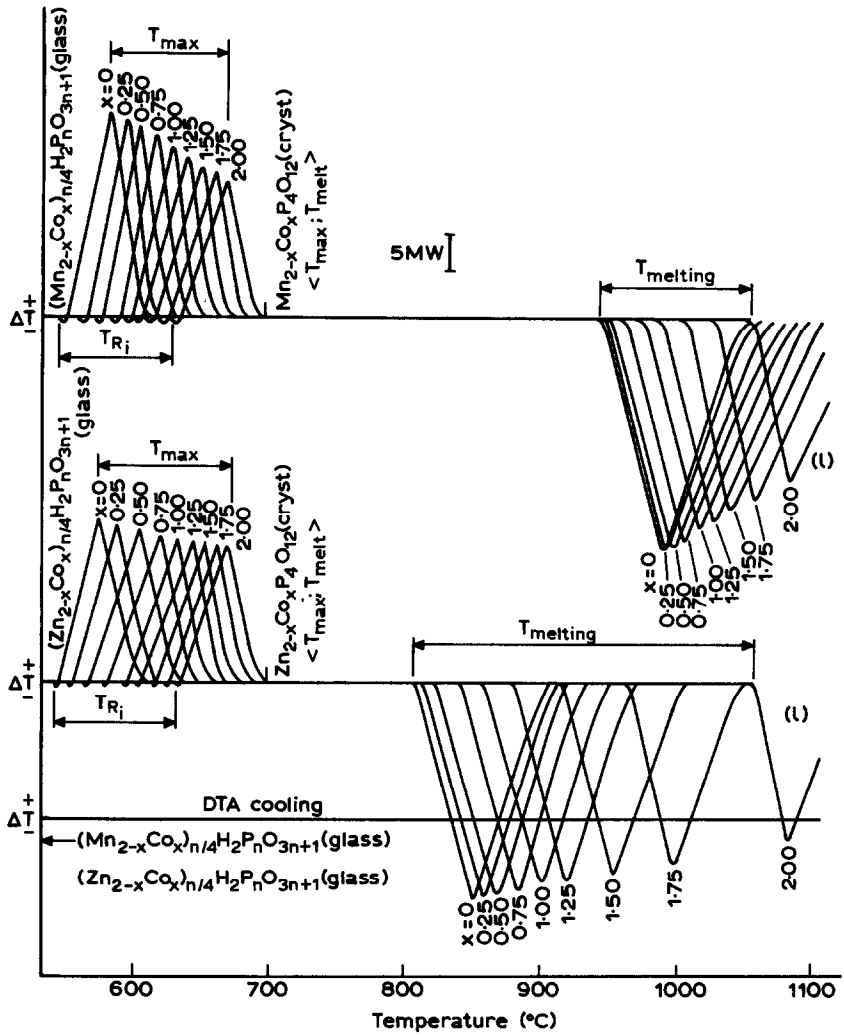

Fig. 1. The DTA curves of the vitreous intermediates $(Mn_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1}$ and $(Zn_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1}$ indicating the formation of the products $Mn_{2-x}Co_xP_4O_{12}$ or $Zn_{2-x}Co_xP_4O_{12}$ (by Scheme 2) and their incongruent melting (Scheme 3). Sample weight, 15 mg; temperature increase, 20°C min^{-1}; Pt-crucible (open); atmosphere; air.

softening and subsequent recrystallization of the amorphous vitreous phase (Scheme 2). The temperatures (T_{Ri}, T_m), heats (ΔH) and yields (α) of this process are summarized in Table 1 and Fig. 2. These values (except ΔH) increase with the content of Co (x) in the products.

The molar ratio P_2O_5/M^{II} + Co in the extracted 0·3 M HCl products varies from 0·9996 to 1·0007 (M^{II} = Mn) and 0·9976 to 1·0020 (M^{II} = Zn); the molar ratio M^{II}/Co corresponds to the values $(2-x)/x$. Each product represents

TABLE 1
The Conditions of Formation of $Mn_{2-x}Co_xP_4O_{12}$ and $Zn_{2-x}Co_xP_4O_{12}$

	x	*0*	*0·25*	*0·5*	*0·75*	*1·0*	*1·25*	*1·5*	*1·75*	*2·0*
T_{Ri} (°C)	Mn–Co	550	565	575	588	598	607	616	625	635
	Zn–Co	545	556	568	583	596	606	618	627	635
T_m (°C)	Mn–Co	583	594	605	616	628	638	651	663	673
	Zn–Co	573	588	605	621	633	643	651	659	673
$-\Delta H$	Mn–Co	175	169	163	157	151	146	140	135	130
($J\,g^{-1}$)	Zn–Co	149	147	144	142	139	137	134	132	130
Yield	Mn–Co	96·6	96·7	96·9	97·1	97·4	97·6	97·9	98·1	98·2
(α; %)	Zn–C0	90·5	90·9	92·1	93·5	95·1	96·7	97·6	97·9	98·2

only a single phase, and its anion corresponds to cyclo-tetraphosphate. Hence, the products are of the type of binary manganese(II)–cobalt(II) or zinc(II)–cobalt(II) cyclo-tetraphosphates of the formula $Mn_{2-x}Co_xP_4O_{12}$ or $Zn_{2-x}Co_xP_4O_{12}$. However, X-ray diffraction analysis showed that no binary products are formed within the whole range of $x \in (0; 2)$ Table 2, Fig. 3).

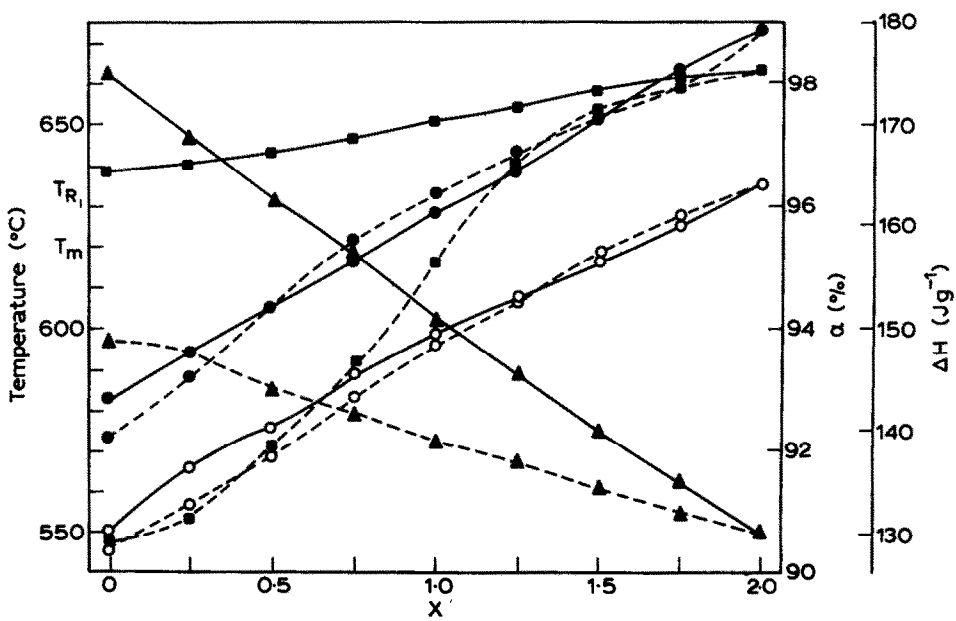

Fig. 2. Data illustrating the reaction in Scheme 2 of formation of $Mn_{2-x}Co_xP_4O_{12}$ (———) and $Zn_{2-x}Co_xP_4O_{12}$ (– – –) and its dependence on the cobalt content (x). T_{Ri}, Temperatures of the beginning of the reaction (○); T_m, temperatures of the maxima of exothermic effects (●); ΔH, heats of the process (▲); α, yields of the process (■).

The structural parameters of the products are slowly but distinctly changed with changing content of cobalt. Their values practically lie in the intervals limited by the structural parameters of the pure simple cyclo-tetraphosphates $Mn_2P_4O_{12}$ and $Co_2P_4O_{12}$ or $Zn_2P_4O_{12}$ and $Co_2P_4O_{12}$. The volume of the elementary cell of the Mn–Co binary products decreases regularly with increasing content of Co, which is in accord with the fact that the ionic radius of cobalt is slightly smaller than that of manganese. In the case of the Zn–Co products, the volumes of the elementary cells change only slightly because the ionic radii of Zn and Co are similar.

As the yields of this synthesis of the binary cyclo-tetraphosphates were high, the sections of the curves above the recrystallization temperature can be taken to determine the thermal stabilities of the binary cyclo-tetraphosphates. The endothermic effects at these DTA curves document

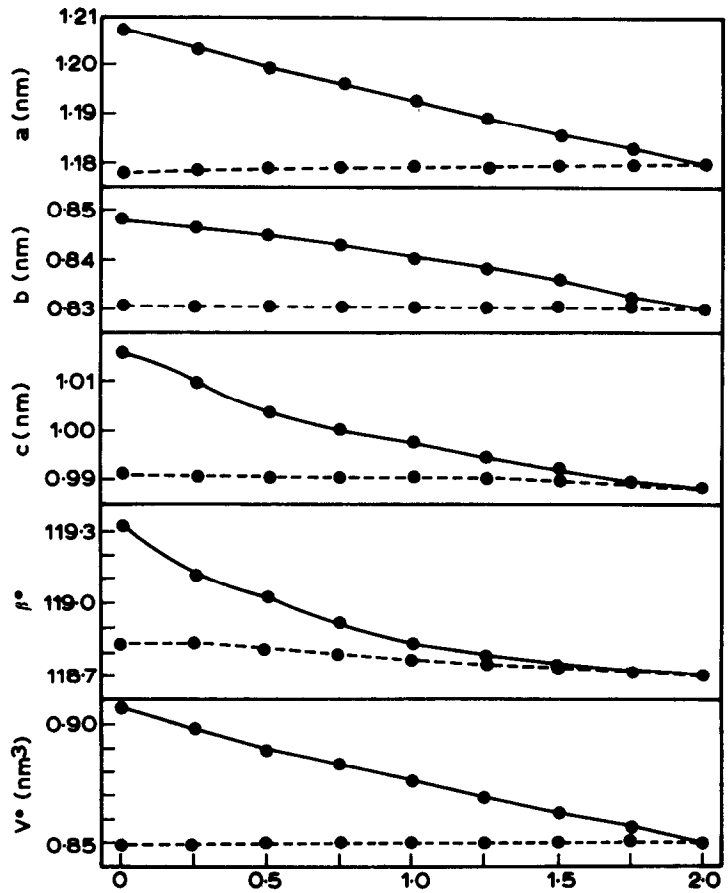

Fig. 3. The structural parameters a, b, c and β and the volume V of the elementary unit cell of $Mn_{2-x}Co_xP_4O_{12}$ (———) and $Zn_{2-x}Co_xP_4O_{12}$ (– – –).

TABLE 2
The Structural Parameters of $Mn_{2-x}Co_xP_4O_{12}$ and $Zn_{2-x}Co_xP_4O_{12}$

	x	*0*	*0·25*	*0·5*	*0·75*	*1·0*	*1·25*	*1·5*	*1·75*	*2·0*
a (nm)	Mn–Co	1·207 6(4)	1·203 2(5)	1·199 2(6)	1·195 8(6)	1·192 4(6)	1·188 9(4)	1·185 4(6)	1·183 1(7)	1·179 9(5)
	Zn–Co	1·177 8(5)	1·178 6(6)	1·179 0(6)	1·179 1(4)	1·179 3(4)	1·179 6(6)	1·179 8(6)	1·179 8(4)	1·179 9(5)
b (nm)	Mn–Co	0·848 4(3)	0·846 7(4)	0·845 2(5)	0·843 3(5)	0·840 9(5)	0·838 4(3)	0·836 0(5)	0·834 1(6)	0·830 4(4)
	Zn–Co	0·830 5(4)	0·830 4(5)	0·830 4(4)	0·830 4(3)	0830 3(3)	0·830 3(5)	0·830 3(4)	0·830 3(3)	0·830 4(4)
c (nm)	Mn–Co	1·015 2(3)	1·009 9(4)	1·003 7(5)	1·000 6(5)	0·997 5(4)	0·994 5(3)	0·991 7(5)	0·989 3(6)	0·988 7 (4)
	Zn–Co	0·991 0(4)	0·990 8(5)	0·990 6(4)	0·990 6(3)	0·990 2(3)	0·990 4(5)	0·989 9(4)	0·989 8(3)	0·988 7(4)
β°	Mn–Co	119·32 (2)	119·12(2)	119·03(3)	118·91(3)	118·84(3)	118·78(2)	118·72(3)	118·71(3)	118·70(3)
	Zn–Co	118·83(3)	118·84(3)	118·81(3)	118·79(2)	118·77(2)	118·75(3)	118·74(3)	118·72(2)	118·70(3)
V_3 (nm)	Mn–Co	0·906 8	0·898 8	0·889 5	0·883 2	0·876 2	0·868 9	0·862 0	0·856 1	0·849 7
	Zn–Co	0·849 2	0·849 4	0·849 8	0·850 1	0·849 9	0·850 4	0·850 3	0·850 3	0·849 7
Δ^a	Mn–Co	0·009	0·010	0·014	0·014	0·013	0·009	0·015	0·015	0·013
	Zn–Co	0·011	0·012	0·013	0·009	0·008	0·010	0·009	0·008	0·013

[a] $\Delta = 1/N\sum_{1}^{N}|2\theta_{exp} - 2\theta_{calc}|$, where $2\theta_{exp}$ is experimental diffraction angle, $2\theta_{calc}$ is the angle calculated from lattice parameters and N is the number of investigated diffraction lines.

$$M^{II}{}_{2-x}Co_xP_4O_{12(cryst.)} + 4/nH_2O_{(g)} = 4/n(M_{2-x}Co_x)_{n/4}H_2P_nO_{3n+1(l)}$$
$$M^{II} = Mn, Zn$$

Scheme 3

their melting (as was confirmed by means of high-temperature microscopy) which is incongruent: the cyclo-tetraphosphates are transformed into higher linear phosphates (Scheme 3), which is favoured by the presence of at least traces of water vapour in the air atmosphere.

Hence, at these conditions the melting temperatures represent the temperatures up to which the binary cyclo-tetraphosphates are stable; with the cobalt content they increase from 950 to 1060°C (Mn–Co) and 810 to 1060°C (Zn–Co) (Table 3, Fig. 4). This fact extends the range of their application to high-temperature purposes.

Also, the density of the binary products continuously changes with the cobalt content: the density values of Mn–Co products increase and those of Zn–Co products decrease with increasing x. The experimental values (ρ_{exp})

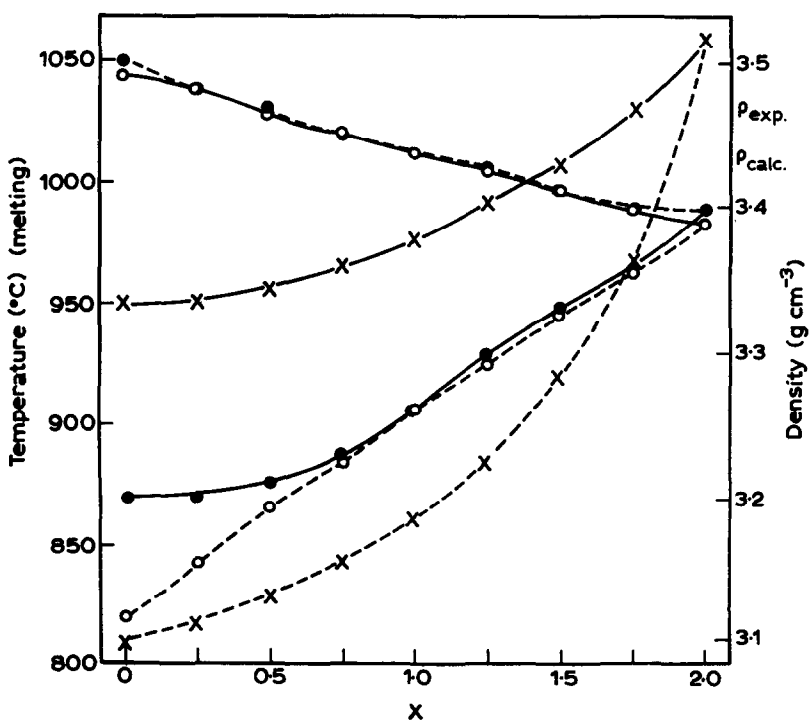

Fig. 4. The dependence of melting temperature (×) and experimental (●) and calculated densities (○) of the products $Mn_{2-x}Co_xP_4O_{12}$ (——) and $Zn_{2-x}Co_xP_4O_{12}$ (– – –) on x.

TABLE 3
Melting Temperature and Densities of $Mn_{2-x}Co_xP_4O_{12}$ and $Zn_{2-x}Co_xP_4O_{12}$

	x	*0*	*0·25*	*0·5*	*0·75*	*1·0*	*1·25*	*1·5*	*1·75*	*2·0*
$T_{melt.}$ (°C)	Mn–Co	950	952	957	965	976	991	1 008	1 030	1 060
	Zn–Co	810	815	828	843	860	884	920	968	1 060
ρ_{exp}	Mn–Co	3·20	3·20	3·21	3·23	3·26	3·30	3·33	3·36	3·40
($g\,cm^{-3}$)	Zn–Co	3·50	3·48	3·47	3·45	3·44	3·43	3·41	3·40	3·40
ρ_{calc}	Mn–Co	3·116	3·153	3·194	3·224	3·258	3·293	3·327	3·358	3·391
($g\,cm^{-3}$)	Zn–Co	3·493	3·480	3·466	3·452	3·440	3·426	3·413	3·401	3·391

are in accord with the density values calculated (ρ_{calc}) on the basis of the X-ray diffraction analysis (Table 3, Fig. 4).

The colour hues of the binary manganese(II)–cobalt(II) cyclo-tetraphosphates and binary zinc(II)–cobalt(II) cyclo-tetraphosphates are intense blue-violet or pink-violet.

CONCLUSION

This paper has shown that it is possible to prepare binary manganese(II)–cobalt(II) cyclo-tetraphosphates $Mn_{2-x}Co_xP_4O_{12}$ and binary zinc(II)–cobalt(II) cyclo-tetraphosphates $Zn_{2-x}Co_xP_4O_{12}$, where $x \in (0;2)$. These intense blue-violet or pink-violet products crystallize in the monoclinic system, C2c group; structural parameters continuously change with the cobalt content. The high thermostability of the products gives the possibility of their application at high-temperature.

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