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Binary cobalt(II)–copper(II) cyclo-tetraphosphates as new colour compounds

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Abstract

The cyclo-tetraphosphates of the type $Co_{2-x}Cu_xP_4O_{12}$, where $x \in (0, 2)$, have been synthesized as new binary compounds. The violet-greenish products crystallize in the monoclinic system (C_{2c}) group) and the structural parameters have the values $a = 1.2546$–1.1799 nm, $b = 0.8092$–0.8304 nm, $c = 0.9565$–0.9887 nm and $\beta = 118.50$–$118.70°$. They were examined for potential applications as special thermostable pigments.

INTRODUCTION

Binary cobalt(II)–copper(II) tetraphosphates with cyclic anions have not yet been described in the literature. In our laboratory, we have synthesized binary (mixed) cyclo-tetraphosphates of some bivalent metals [1–3]. These new compounds have been evaluated with respect to their application as special inorganic pigments.

EXPERIMENTAL METHODS

The procedure suggested by us for preparation of binary cobalt–copper cyclo-tetraphosphates is based on a two-step thermal synthesis [4]. 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 general formula $(Co_{2-x}Cu_x)_{n/4}H_2P_nO_{3n+1}$. In the second step the product is heated repeatedly to a suitable temperature and recrystallized to give a microcrystalline product $Co_{2-x}Cu_2P_4O_{12}$.

The starting simple cyclo-tetraphosphates were prepared on the basis of the thermal method described in ref. 5. In our laboratory this procedure

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was modified [6] so as to obtain as pure as possible cyclo-tetraphosphates [1] (see Scheme 1).

$$M^{II}CO_3 + 2H_3PO_4 \xrightarrow{120(170)^\circ C} M(H_2PO_4)_2 \xrightarrow{205(260)^\circ C}$$

$$MH_2P_2O_7 \xrightarrow{310(325)^\circ C} M_2P_4O_{12}$$

$M^{II} = Co(Cu), p_{H_2O} \approx 100\,kPa\,(g)$

Scheme 1

The synthesis of $Co_{2-x}Cu_xP_4O_{12}$ was given in ref. 2 and is shown in Scheme 2.

$$(1 - 0.5x)Co_2P_4O_{12}(c) + 0.5xCu_2P_4O_{12}(c) + (4/n)H_2O \xrightarrow[\text{air atmosphere}]{\text{melting (810–850)}^\circ C}$$

$$(4/n)(Co_{2-x}Cu_x)_{n/4}H_2P_nO_{3n+1}(l) \xrightarrow[\text{(solidification)}]{950 \rightarrow 25^\circ C}$$

$$(4/n)(Co_{2-x}Cu_x)_{n/4}H_2P_nO_{3n+1}(gl) \xrightarrow{T\,\text{(recryst.)}} Co_{2-x}Cu_xP_4O_{12} + (4/n)H_2O$$

Scheme 2

The values of x equal 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 by heating in an electric furnace to 1100°C. After 30 min, the dishes with the melts were removed from the furnace and cooled rapidly by immersion in water. The obtained vitreous products $(Co_{2-x}Cu_x)_{n/4}H_2P_nO_{3n+1}$ 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 determine the temperatures and heats of the exothermic processes of thermal recrystallization (temperatures T_{Ri} and T_{max}, ΔH). The individual intermediates were then calcinated in the electric furnace at temperatures 10°C higher (T_{max} + 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 ($\propto$) were determined by a special analytical extraction method [7].

The starting cyclo-tetraphosphates, the vitreous amorphous intermediates and the final products were analysed by the instrumental analytical methods described in our previous papers [1–3].

RESULTS AND DISCUSSION

Figure 1 presents the DTA curves; the first sections indicate an exothermic process which represents the reaction of the formation of the binary cyclo-tetraphosphate from the higher linear phosphates intermediate, which is associated with the recrystallization of the amorphous vitreous

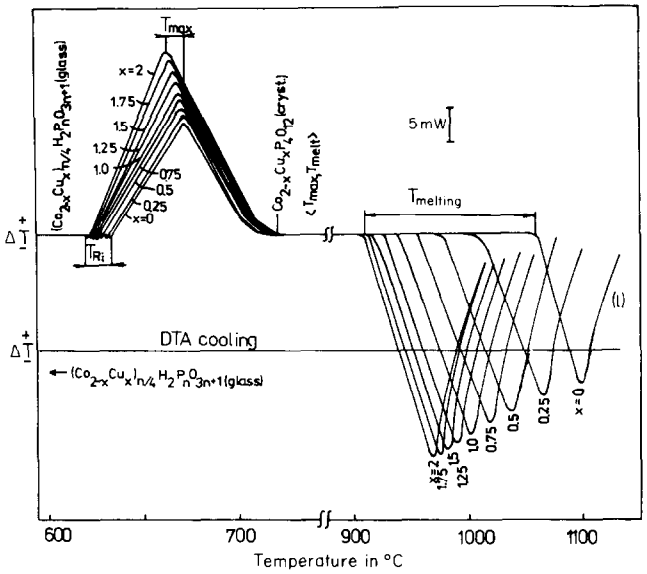

Fig. 1. The DTA curves of the vitreous intermediates $(Co_{2-x}Cu_x)_{n/4}H_2P_nO_{n+1}$, indicating the formation of the products $Co_{2-x}Cu_xP_4O_{12}$ (by reaction (2)) and their incongruent melting (3). DTA-1700 apparatus with DSC Mode (Perkin-Elmer), sample weight 15 mg, temperature increase 20°C min^{-1}, Pt crucible (open), and air atmosphere.

phase [2]. The temperatures (T_{Ri}, T_{max}) of this process, as determined from the DTA results, fluctuate slightly with increasing copper content (the heats ΔH increase regularly, see Table 1).

The yields (α) of the synthesis are high and decrease with increasing copper content. The molar ratio $P_2O_5/(Co + Cu)$ in the extracted (0.3 M HCl) products varies from 0.99 to 1.0022, and the molar ratio Co/Cu corresponds very precisely to the values $(2 - x)/x$. Each product represents only a single phase, and its anion corresponds to cyclo-tetraphosphate. Hence, the products are of the type of binary cobalt(II)–copper(II) cyclo-tetraphosphates of formula $Co_{2-x}Cu_xP_4O_{12}$, which applies to the whole range of $x \in (0, 2)$.

As the yields of the synthesis were high, the sections of the DTA curves

TABLE 1

The parameters of formation of $Co_{2-x}Cu_xP_4O_{12}$

	x								
	0	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0
T_{Ri}/°C	635	634	632	631	629	628	627	626	625
T_{max}/°C	673	673	670	668	666	666	664	663	662
$-\Delta H$/(J g^{-1})	130	138	146	153	161	169	178	188	190
α/(%)	98.2	97.9	97.6	97.2	96.5	96.0	95.4	94.8	94.2
T_{melt}/°C	1060	1010	978	956	939	927	918	913	910

above the recrystallization temperature can be applied to the determination of the thermal stability of the binary cyclo-tetraphosphates. The endothermic effects of these DTA curves document their melting (as confirmed by high-temperature microscopy) which is incongruent: the cyclo-tetraphosphates are transformed into higher linear phosphates [3], which is favoured by the presence of at least traces of water vapour in the air atmosphere [8]

$$Co_{2-x}Cu_xP_4O_{12}(c) + (4/n)H_2O(g) = (4/n)(Co_{2-x}Cu_x)_{n/4}H_2P_nO_{3n+1}(l)$$

Hence, under these conditions, the melting temperatures represent the temperatures up to which the binary cyclo-tetraphosphates are stable; with increasing copper content, they decrease from 1060 to 910°C (Fig. 1, Table 1). This demonstrates the high thermal stability of the products, which extends the range of their application to high-temperature purposes.

The structural parameters of the products (Table 2, Fig. 2) slowly but noticeably fluctuate with increasing proporitions of copper. The values of *a*, *b*, and *c* lie practically within the intervals limited by the structural parameters of the pure single cyclo-tetraphosphates $Co_2P_4O_{12}$ and $Cu_2P_4O_{12}$. The volume of the elementary cell (and also the angle β) of the

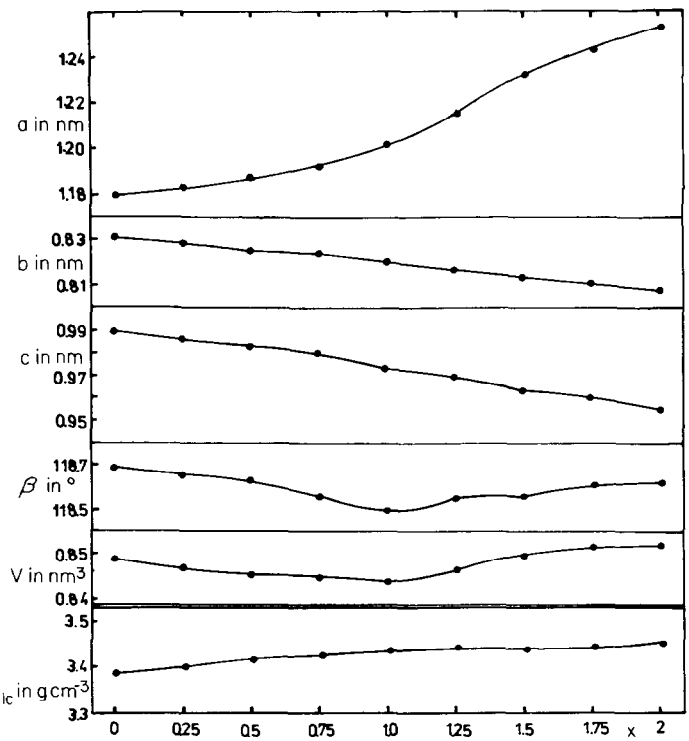

Fig. 2. The structural parameters *a*, *b*, *c* and β, and volume *V* of the elementary unit cell, and the density calculated ρ_{calc} of $Co_{2-x}Cu_xP_4O_{12}$.

TABLE 2

The structural parameters (and calculated density) of the $Co_{2-x}Cu_xP_4O_{12}$ products

	x								
	0	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0
a/nm	1.1799(5)	1.1825(5)	1.1868(8)	1.1922(7)	1.2027(4)	1.2169(7)	1.2338(5)	1.2446(7)	1.2546(7)
b/nm	0.8304(4)	0.8282(4)	0.8248(6)	0.8239(5)	0.8202(3)	0.8169(5)	0.8138(4)	0.8108(5)	0.8092(5)
c/nm	0.9887(4)	0.9863(4)	0.9841(6)	0.9810(5)	0.9737(3)	0.9706(5)	0.9641(4)	0.9613(5)	0.9565(5)
β/deg	118.70(3)	118.67(2)	118.62(4)	118.56(3)	118.50(2)	118.56(3)	118.56(3)	118.62(3)	118.63(3)
V/nm^3	0.8497	0.8476	0.8462	0.8456	0.8441	0.8473	0.8504	0.8521	0.8523
Δ [a]	0.013	0.011	0.016	0.013	0.011	0.01	0.013	0.019	0.016
$\rho_{calc}/(g\ cm^{-3})$	3.391	3.408	3.423	3.434	3.439	3.445	3.442	3.444	3.452

[a] $\Delta = 1/N \sum_1^N |2\theta_{exp} - 2\theta_{calc}|$, where $2\theta_{exp}$ is the experimental diffraction angle, $2\theta_{calc}$ is the angle calculated from the lattice paramters and N is the number of investigated diffraction lines.

binary products is almost the same over the whole range of x, which is in accordance with the fact that the ionic radius of cobalt and copper are similar.

The densities (calculated on the basis of the X-ray diffraction analysis) of the binary products (Table 2) change slightly, yet continuously, with the copper content; the density values increase with increasing x. The experimentally determined density values (pycnometer method) are very similar and lie in the interval 3.43–3.45 g cm^{-3}.

The colour of the binary cobalt(II)–copper(II) cyclo-tetraphosphates is intense blue–violet to greenish, the blue–violet hue decreasing with increasing copper content of the product.

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