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Short Communication

Binary Cu(II)–Mn(II) cyclo-tetraphosphates

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Abstract

Cyclo-tetraphosphates of the type $Cu_{2-x}Mn_xP_4O_{12}$ have been synthesised as new binary compounds. The synthesis is based on a thermal procedure involving the reversible transformation of cyclo-tetraphosphates to higher linear phosphates. The compounds prepared have been evaluated from the standpoint of their structure, density and thermal stability.

Keywords: Condensed phosphates; Binary cyclo-tetraphosphates; Copper; Manganese; Inorganic pigments

1. Introduction

Cyclo-tetraphosphates of some divalent metals have been prepared in our laboratory and examined for potential use as special inorganic pigments [1,2]. This work is of interest because it appears economically advantageous to substitute a portion of the divalent metal with a less costly divalent element that could also improve, in some cases, special pigment properties. Such a suitable element, from our experiences, is manganese, which alone does not give a cyclo-tetraphosphate [3]. Therefore, binary copper–manganese tetraphosphates containing cyclic anions have not been described in the literature to date. With this in mind, we examined the possibility of preparing binary Cu(II)–Mn(II) tetraphosphates by a thermal procedure developed in our laboratory in other studies [4].

It was anticipated that thermal analyses could be used to detect and explain the processes that accompany the melting and recrystallization of the cyclo-tetraphosphates.

2. Experimental

The synthesis of the binary cyclo-tetraphosphates was conducted according to the following procedure developed in our laboratory. The method used to the prepare $Cu_{2-x}Mn_xP_4O_{12}$ involved a two-step thermal process. In the first step, the mixtures of copper and manganese cyclo-tetraphosphates were melted together on platinum dishes in an electric furnace by heating at 1000°C, i.e. above the melting temperatures of $Mn_2P_4O_{12}$ (950°C) and $Cu_2P_4O_{12}$ (910°C) [5,6], in an atmosphere containing air. The reaction mixtures were cooled abruptly to give a vitreous product composed of higher linear phosphates

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$$M^{II}CO_3 + 2\,H_3PO_4 \rightarrow M(H_2PO_4)_2 + H_2O + CO_2 \qquad 135°C\ (120°C)$$

$$M(H_2PO_4)_2 \rightarrow MH_2P_2O_7 + H_2O \qquad 300°C\ (205°C)$$

$$MH_2P_2O_7 \rightarrow 1/2\,M_2P_4O_{12} + H_2O \qquad 405°C\ (310°C)$$

Scheme 1. Three-stage synthesis of pure cyclo-tetraphosphates.

$(Cu_{2-x}Mn_x)_{n/4}H_2P_nO_{3n+1}$, where the values of x were 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0.

The vitreous products were dried at 105°C and ground in a vibrating pebble mill. Aliquots of these intermediates were then subjected to DTA to determine T_{Ri}, T_{max} and ΔH of thermal recrystallization, where T_{Ri} is the temperature at which $Cu_{2-x}Mn_xP_4O_{12}$ formation begins and T_{max} is the maximum temperature for this exothermic process. The individual intermediates were then calcinated in the electric furnace at 20°C above T_{max} for 30 min, to give the microcrystalline product $Cu_{2-x}Mn_xP_4O_{12}$. The sintered blocks of the individual final products obtained in this way were ground in the vibrating pebble mill.

The yields of the process were determined by a special analytical extraction method [7]. Extraction of the calcinates with 0.3 M HCl was used to determine the temperature ranges associated with incomplete conversion of starting compounds [8,9] and the degree of conversion of calcinates to final products.

The starting cyclo-tetraphosphates, vitreous amorphous intermediates and final products were analysed by X-ray diffraction. Structural parameters for the final products were determined using Cu$K\alpha\lambda = 0.154178$ nm and an HZG-4B diffractometer (Germany). The diffractograms were indexed under the asumption that the mixed cyclo-tetraphosphates were isostructural [10] with $Cu_2P_4O_{12}$ and $Mn_2P_4O_{12}$. The lattice parameters of the monoclinic unit cell (C2c group) were calculated by the least square's method.

The final products were also subjected to pycnometric analysis to estimate their densities and their optical reflectance in the visible region.

3. Results and discussion

The principal goal of this work was to develop conditions for the synthesis of mixed cyclo tetraphosphates of the type $Cu_{2-x}Mn_xP_4O_{12}$. The starting cyclo-tetraphosphates were prepared by using the three-stage synthetic sequence shown in Scheme 1. The conditions listed gave optimum purity in the cyclo-tetraphosphates, where $M^{II} = Cu$ (Mn). The synthesis of the mixed cyclo-tetraphosphates was carried out according to the three-stage process shown in Scheme 2, where the temperatures given in parentheses were used in preparing the Mn products.

Using DTA [11], it was found that an exothermic process characterizes the formation of the binary cyclo-tetraphosphate from an intermediate linear phosphate, and that formation of the latter occurs via recrystallization of the amorphous vitreous phase. From Table 1, it is clear that the temperature (T_{Ri}, T_{max}) and ΔH values decrease with increasing Mn content of manganese, while the yields for this process increase with increasing Mn content.

$$(1 - x/2)\,Cu_2P_4O_{12}\ (cryst.) + x/2\,Mn_2P_4O_{12}(cryst.) + 4/n\,H_2O \rightarrow 4/n\,(Cu_{2-x}Mn_x)_{n/4}H_2P_nO_{3n+1}\ (l)$$
(1000°C, melting in air)

$$4/n\,(Cu_{2-x}Mn_x)_{n/4}H_2P_nO_{3n+1}\ (l) \rightarrow 4/n\,(Cu_{2-x}Mn_x)_{n/4}H_2P_nO_{3n+1}\ (glass)$$
(1000–25°C, solidification)

$$4/n\,(Cu_{2-x}Mn_x)_{n/4}H_2P_nO_{3n+1}\ (glass) \rightarrow Cu_{2-x}Mn_xP_4O_{12}\ (cryst.) + 4/nH_2O$$
(T_{Ri}, recrystallization)

Scheme 2. Three-stage preparation of mixed cyclo-tetraphosphates.

The P_2O_5/(Cu + Mn) molar ratio in the extracted (0.3M HCl) product varies from 0.9991 to 1.0003, and the Cu/Mn molar ratio correlates very closely to the values of $(2-x)/x$. Each product was a single-phase binary copper (II)–manganese (II) cyclo-tetraphosphate material of the formula $Cu_{2-x}Mn_xP_4O_{12}$. These results apply to the whole range of $x \in (0,2)$.

The structural parameters b, c, angle β and V (the volume of the elementary unit cell) of the products (Table 2) slowly but clearly decrease with increasing proportion of Mn. Parameter a increases from 1.2076(4) to 1.2546(1) nm with increasing Mn content in the product. Their values practically lie in the intervals limited by the structural parameters of the pure simple cyclo-tetraphosphates ($Cu_2P_4O_{12}$ and $Mn_2P_4O_{12}$). The volume of the elementary cell of the binary products changes only slightly because the ionic radius of copper ($r[Cu^{2+}] = 0.075$ nm) is slightly smaller than that manganese ($r[Mn^{2+}] = 0.083$ nm).

Table 1
Experimental data for $Cu_{2-x}Mn_xP_4O_{12}$ pigments

x	T_{Ri} (°C)	T_{max} (°C)	$-\Delta H$ (J.g^{-1})	Yield (%)
0	625	662	190	94.2
0.25	616	653	189	94.5
0.50	606	642	187	94.9
0.75	597	631	185	95.1
1.00	588	623	183	95.4
1.25	579	614	180	95.8
1.50	570	603	178	96.1
1.75	561	594	176	96.4
2.00	550	583	175	96.6

Table 2
Structural parameters for $Cu_{2-x}Mn_xP_4O_{12}$ pigments

x	a (nm)	b (nm)	c (nm)	β (°)	V (nm^3)	$\Delta 2v$[a]
0	1.2076(4)	0.8474(3)	1.0152(3)	119.32(2)	0.9068	0.009
0.25	1.2054(2)	0.8450(2)	1.0076(2)	119.14(2)	0.8964	0.005
0.50	1.2039(2)	0.8417(2)	0.9943(3)	119.02(2)	0.8611	0.009
0.75	1.2076(3)	0.8362(3)	0.9866(3)	118.92(3)	0.8720	0.009
1.00	1.2146(3)	0.8321(3)	0.9826(3)	118.81(3)	0.8702	0.012
1.25	1.2280(2)	0.8226(2)	0.9743(2)	118.73(2)	0.8630	0.007
1.50	1.2356(4)	0.8163(4)	0.9664(4)	118.69(3)	0.8551	0.011
1.75	1.2463(2)	0.8115(2)	0.9620(2)	118.61(2)	0.8541	0.006
2.00	1.2546(7)	0.8092(5)	0.9565(5)	118.63(3)	0.8523	0.016

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

Some physical properties of the pigment products were determined (Table 3), with the potential use of the products as anticorrosive pigments in mind. As the yields of pigment synthesis were high, the sections of DTA curves above the recrystallization temperature could be used to estimate the thermal stabilities of the formed cyclo-tetraphosphates. The endothermic effects observed in DTA curves were consistent with results of high-temperature microscopy and indicate that true melting does not occur. Rather, along with melting, the cyclo-tetraphosphates are transformed into higher linear phosphates, a process that is favoured by the presence of at least traces of water vapour in the atmosphere. Hence, the melting temperatures represent the temperatures up to which the binary cyclo-tetraphosphates are stable and above which linear phosphate formation occurs. The melting temperatures increase from 910 to 950°C, with increasing Mn content. This indicates that the present pigments are suitable for high-temperature applications.

It is also clear that the densities of the binary copper (II)–manganese (II) cyclo-tetraphosphates changes with Mn content. However, as would be expected, the density values increase as x increases, with good agreement between $\rho_{exp.}$ and $\rho_{calc.}$ (from X-ray diffraction).

Table 3
Melting temperatures and densities for $Cu_{2-x}Mn_xP_4O_{12}$ pigments

x	$T_{melting}$ (°C)	$\rho_{exp.}$ (g. cm^{-3})	$\rho_{calc.}$ (g. cm^{-3})
0	910	3.20	3.119
0.25	916	3.21	3.171
0.50	922	3.26	3.242
0.75	927	3.28	3.292
1.00	931	3.32	3.316
1.25	938	3.35	3.360
1.50	942	3.38	3.407
1.75	947	3.42	3.428
2.00	950	3.44	3.452

The hues of the binary products are green to yellowish green, with the intensity of the hues decreasing with increasing Cu content. The modest colour value of these products, especially when the Mn content is high, is advantageous for their application as heat stable anticorrosive pigments. This means that coatings containing these anticorrosive pigments may be easily coloured to the desired hue using the more economical traditional pigments.

4. Conclusions

The results if this study show that it is possible to prepare green or yellowish green binary copper(II)–manganese(II) cyclo-tetraphosphates (Cu_{2-x} $Mn_xP_4O_{12}$) in which the color is determined by Cu and Mn content. The products crystalize in the monoclinic system, C2c group, and their structure parameters vary with Mn content. The melting temperatures of the new pigments increase with increasing Mn content, giving the possibility of their use at high temperatures.

References

[1] Trojan M, Brandová D, Šolc Z. Thermochim Acta 1987;110:343.
[2] Trojan M, Šolc Z. J Thermal Anal 1987;32:1707.
[3] Thilo E, Grunze HZ. Anorg Allg Chem 1959;290:209.
[4] Trojan M. Czech Patent 1986;449:247.
[5] Trojan M. Mat Letters 1989;8:247.
[6] Trojan M, Beneš L. Mat Letters 1989;8:324.
[7] Trojan M, Brandová D. Czech Patent 1984;232:090.
[8] Trojan M, Brandová D. Thermochim Acta 1986;80:541.
[9] Trojan M. Chem Listy 1986;80:541.
[10] Begieu-Beucher M, Condrand M, Perroux M. J Solid State Chem 1976;19:359.
[11] Málek J, Klikorka J. J Thermal Anal 1987;32:1883.