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Chemical Preparations and X-ray Diffraction Data of Cyclotriphosphates Type $MnM^{II}_2(P_3O_9)_2.nH_2O$ with M^{II} Alkaline Earths

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Abstract: Chemical preparation methods and X-ray powder diffraction data, XPRD, are reported for four cyclotriphosphates associated with manganese $MnM^{II}_2(P_3O_9)_2.nH_2O$ with M^{II} alkaline earths. These phosphates are $MnCa_2(P_3O_9)_2.10H_2O$, $MnCa_2(P_3O_9)_2$, $MnSr_2(P_3O_9)_2.4H_2O$ and $MnBa_2(P_3O_9)_2.6H_2O$. The condensed phosphates $MnSr_2(P_3O_9)_2.4H_2O$ and $MnBa_2(P_3O_9)_2.6H_2O$ were prepared by the method of ion-exchange resin, whereas $MnCa_2(P_3O_9)_2.10H_2O$ was prepared by using nitrates and $MnCa_2(P_3O_9)_2$ was obtained by total thermal dehydration of $MnCa_2(P_3O_9)_2.10H_2O$. $MnSr_2(P_3O_9)_2.4H_2O$ crystallizes in the triclinic system, space group is P-1, Z = 1, the unit-cell parameters are : a = 6,653(1)Å, b = 7,110(1)Å, c = 5,123(1)Å, α = 103,37(2)°, β = 95,81(2)°, γ = 93,04(2)° and the factors of merit, M(20) = 29.6 and F(30) = 34.4. $MnCa_2(P_3O_9)_2.10H_2O$ crystallizes in the monoclinic system, space group is $P2_1/n$, the unit-cell parameters of $MnCa_2(P_3O_9)_2.10H_2O$ are : a = 9.631 (5) Å, b = 18.173 (7) Å, c = 7.976 (4) Å, β = 109.438 (4), Z = 2 and V = 1045,1 (3) $Å^3$. $MnCa_2(P_3O_9)_2$ an hexagonal symetry, Z = 2, the space group is P3 and the unit-cell parameters are a = 7.392 Å (9) and c = 20.134 (2) Å. $MnBa_2(P_3O_9)_2.6H_2O$ crystallizes in the triclinic unit cell, , Z = 2, the space group is P-1 and its unit-cell parameters are : a = 7,479 (6)Å, b = 11,942 (8)Å, c = 12,786 (9)Å, α = 105,94(7)°, β = 98,40°(7), γ = 98,16 (7)° and V = 1046,8 (2)$Å^3$.

Keywords: chemical preparation; powder; cyclotriphosphate; alkaline earths; manganese; X-Ray diffraction.

1. Introduction

In recent years, phosphates have been widely studied due to their important and diverse industrial uses, including as optical materials [1-2], thermal protection coatings (R. P. Rao et al. 2000), UV coatings [3-4], catalysis [5-6] and corrosion inhibitors [7-8]. Inorganic phosphates are perhaps one of the most interesting types of new inorganic materials, mainly because of the ability of the P_3O_9 group to chemically interact with other structural units. Given their importance in several application areas, particularly in medicine, we have been interested in this type of anion to synthesize new materials associated with inorganic cations. During our investigation, we were interested in a new series of cyclotriphosphates associated with manganese $MnM^{II}_2(P_3O_9)_2.nH_2O$ with alkaline earths M^{II}, of which only one of this type,

whose structure is solved $ZnBa_2(P_3O_9)_2.10H_2O$, is known until today. These four phosphates have the formula $MnM^{II}_2(P_3O_9)_2.nH_2O$ (M^{II} = Ca, n = 10 and 0; M^{II} = Sr, n = 4 and M^{II} = Ba, n = 6) To our knowledge, the crystal structure of any of these four phosphates, has not been reported.

2. Materials and Methods

2.1. Chemical preparation.

2.1.1. $MnSr_2(P_3O_9)_2.4H_2O$.

Through a column of ion exchange resin (Na^+ by H^+), "Amberlite IR 120" [9-10], a concentrated solution of $Na_3P_3O_9$ is slowly added to form $H_3P_3O_9$. The cyclotriphosphoric acid $H_3P_3O_9$ thus obtained is immediately neutralized by mixing stoichiometric quantities of manganese carbonate, $MnCO_3$ and strontium carbonate, $SrCO_3$, according to the following chemical reaction:

$$2H_3P_3O_9(l) + 2SrCO_3(s) + 1MnCO_3(s) + H_2O(l) \longrightarrow MnSr_2(P_3O_9)_2.4H_2O(l) + 3CO_2(g)$$

The resulting filtrate is kept under mechanical agitation for 24 hours. After filtration, the solution was left for two weeks for spontaneous evaporation, $MnSr_2(P_3O_9)_2.4H_2O(s)$ is obtained as a pink-colored $Na_3P_3O_9$ was obtained by heat treatment of sodium dihydrogenomonophosphate, NaH_2PO_4, at 530°C for 5 hours at atmospheric pressure according to the following chemical reaction :

$$3NaH_2PO_4\ (s) \longrightarrow Na_3P_3O_9\ (s) + 3H_2O\ (g)$$

2.1.2. $MnBa_2(P_3O_9)_2.6H_2O$.

A similar experimental protocol was used to prepare $MnBa_2(P_3O_9)_2.6H_2O(l)$.

$$2H_3P_3O_9(l) + 2BaCO_3(s) + 1MnCO_3(s) + 3H_2O(l) \longrightarrow MnBa_2(P_3O_9)_2.6H_2O(l) + 3CO_2(g)$$

The spontaneous evaporation, under atmospheric pressure, which took six weeks led to $MnBa_2(P_3O_9)_2.6H_2O(s)$ with a similar pink color of $MnSr_2(P_3O_9)_2.4H_2O$

2.1.3. $MnCa_2(P_3O_9)_2.10H_2O$.

Manganese calcium cyclotriphosphate decahydrate, $MnCa_2(P_3O_9)_2.10H_2O$ [11] was prepared using manganese and calcium nitrates. To an aqueous solution of the anhydrous sodium cyclotriphosphate $Na_3P_3O_9$ (3.059 g $Na_3P_3O_9$ in 60 ml of distilled water) is added in stoichiometric quantities and with mechanical stirring, a mixture in an aqueous solution containing calcium nitrate tetrahydrate (2.362 g $Ca(NO_3)_2.4H_2O$), manganese nitrate tetrahydrate (1.255 g of $Mn(NO_3)_2.4H_2O$) and 60 ml of distilled water. The mixture of the aqueous nitrate solution has a pink color. Mechanical agitation is maintained for 24 hours at room temperature. After filtration, the solution thus obtained can be treated in two ways: either evaporated slowly at room temperature or drip-fed with ethyl alcohol while maintaining strong mechanical agitation. In the first case, a well-crystallized product is obtained, but it is not possible to grow single crystals of the appropriate size for a structural study. In the second case, after a few minutes at room temperature, a well-crystallized light pink powder is obtained. The chemical reaction is as follows:

$$2Na_3P_3O_9(l)+Mn(NO_3)_2.4H_2O(l)+2Ca(NO_3)_2.4H_2O(l) \longrightarrow MnCa_2(P_3O_9)_2.l0H_2O(s) + 6NaNO_3(l) + 2H_2O(l)$$

2.1.4. $MnCa_2(P_3O_9)_2$.

The total thermal dehydration of $MnCa_2(P_3O_9)_2.l0H_2O$ under [11-15] atmospheric pressure at 400°C leads to the corresponding anhydrous $MnCa_2(P_3O_9)_2$.

All the phases prepared, $MnSr_2(P_3O_9)_2.4H_2O$, $MnBa_2(P_3O_9)_2.6H_2O$, $MnCa_2(P_3O_9)_2.l0H_2O$ (s) and $MnCa_2(P_3O_9)_2$ are stable under the ambient conditions of pressure and temperature.

2.2. Characterization technique.

2.2.1. X-ray powder diffraction measurements.

Diffraction data were collected at room temperature on a D2 Phaser Diffractometer, with the Bragg-Brentano geometry, using Cu Kα radiation (λ = 1,5418Å) with 30 kV and 10 mA. The patterns were scanned through steps of 0,01° (2θ) in the 2θ range 2-70°, counting time 30 s, with the sample spinner.

3. Results and Discussion

3.1. $MnSr_2(P_3O_9)_2.4H_2O$.

$MnSr_2(P_3O_9)_2.4H_2O$ has no isotypic compound. An automatic indexation using the Dicvol and Treor programs [16-20] showed that this cyclotriphosphate crystallizes in a triclinic space group is P-1 and Z = 1. The unit-cell parameters calculated and refined by the least-squares method are: a = 6,653(1)Å, b = 7,110(1)Å, c = 5,123(1)Å, α = 103,37(2)°, β = 95,81(2)°, γ = 93,04(2)°. The figures of merit, M(20) =29.6 and F(30) = 34.4, of $MnSr_2(P_3O_9)_2.4H_2O$, were calculated using the computer program Treor [21-24], The X-ray powder diffraction pattern for $MnSr_2(P_3O_9)_2 \cdot 4H_2O$ is reported in Figure 1. Indexing of the X-ray powder diffraction pattern for $MnSr_2(P_3O_9)_2.4H_2O$ is given in Table 1.

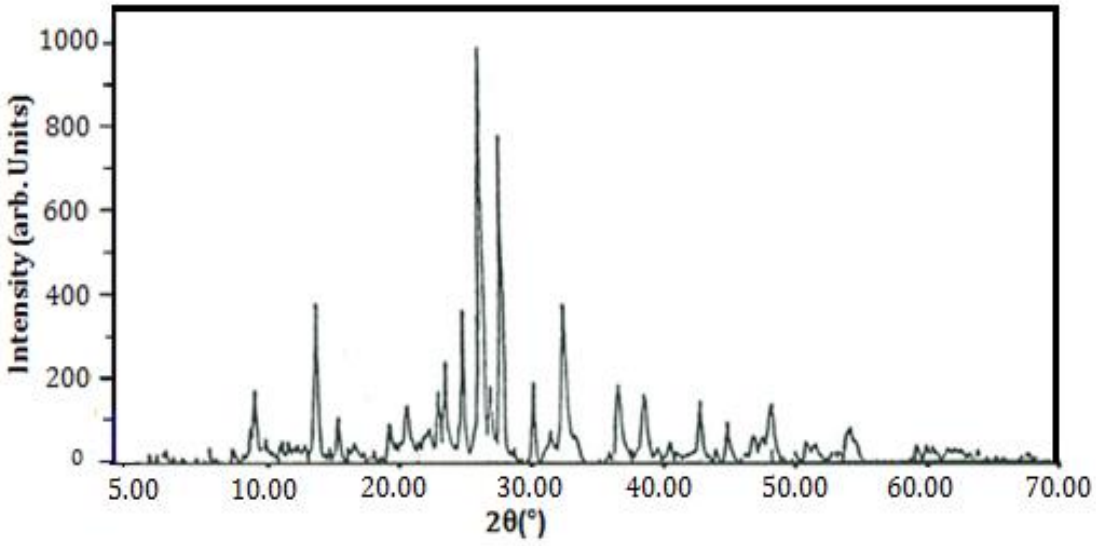

Figure 1. X-ray powder diffraction pattern for $MnSr_2(P_3O_9)_2 \cdot 4H_2O$.

Table 1. Indexing of the X-ray powder diffraction pattern for $MnSr_2(P_3O_9)_2.4H_2O$.

2θobs (°)	dobs (Å)	100I/I0	hkl	2θcal (°)	dcal(Å)	Δ2θ
6,7126	6,59	16	100	6,7126	6,59	0
17,6467	2,541	34	021	17,5468	2,555	0,0999
8,9343	4,96	34	-110	9,6611	4,59	-0,7268
9,7038	4,57	10	01-1	9,7038	4,57	0
18,1410	2,474	05	002	18,1410	2,474	0
11,5172	3,858	09	11-1	11,5202	3,857	-0,003
19,5671	2,300	17	211	19,5671	2,300	0
12,1428	3,662	13	-11-1	12,1428	3,662	0
20,5053	2,199	15	300	20,4761	2,202	0,0292
21,3270	2,118	05	130	21,3905	2,112	-0,0635
12,9166	3,446	08	31-1	22,4163	2,020	-9,4997
22,3464	2,026	14	020	12,9128	3,447	9,4336
13,2331	3,365	16	-111	13,2331	3,365	0
23,4073	1,939	09	-31-1	23,4714	1,934	-0,0641
13,5070	3,298	22	200	13,4903	3,302	0,0167
24,3673	1,867	07	23-1	24,3812	1,866	-0,0139
24,7630	1,839	06	13-2	24,7057	1,843	0,0573
14,1225	3,157	33	-120	14,1043	3,161	0,0182
25,0392	1,820	13	230	25,0099	1,822	0,0293
26,2113	1,744	15	-230	26,2275	1,743	-0,0162
14,7674	3,022	200	111	14,7524	3,025	0,015
26,5390	1,724	04	040	26,4728	1,728	0,0662
15,0788	2,961	16	120	15,0736	2,962	0,0052
26,6056	1,720	05	-14-1	26,5722	1,722	0,0334
27,5935	1,663	06	-330	27,6296	1,661	-0,0361
24,0654	1,889	69	12-1	15,4529	2,891	8,6125
27,7566	1,654	08	-312	27,7748	1,653	-0,0182
28,0143	1,640	04	140	27,9957	1,641	0,0186
30,0989	1,536	04	-420	30,0773	1,537	0,0216
16,2788	2,748	17	21-1	16,5828	2,699	-0,304
30,4491	1,520	04	041	30,4270	1,521	0,0221
30,6275	1,512	04	222	30,6275	1,512	0
17,2267	2,601	0.8	201	17,1858	2,607	0,0409

2 Theta range:5-70°(2θ), Step size: 0.01°(2θ), Counting time: 30 s

3.2. $MnCa_2(P_3O_9)_2.10H_2O$.

$MnCa_2(P_3O_9)_2.10H_2O$ is isotype to the series of cyclotriphosphates $M^{II}_3(P_3O_9)_2.10H_2O$ (M^{II} = Cd, Mn, Ca) [25-26]**,** and crystallizes in the monoclinic system, space group $P2_1/n$. The unit-cell parameters of $MnCa_2(P_3O_9)_2.10H_2O$ were calculated and refined by isotopy with the series $M^{II}_3(P_3O_9)_2.10H_2O$ (M^{II} = Cd, Mn, Ca) [25-26]**.**The unit-cell parameters are : a = 9.631 (5) Å, b = 18.173 (7) Å, c = 7.976 (4) Å, β = 109.438 (4), Z = 2 and V = 1045,1 (3) $Å^3$ [27]**.**The X-ray powder diffraction pattern for $MnCa_2(P_3O_9)_2 \cdot 10H_2O$ is reported in Figure 2. Indexing of the X-ray powder diffraction pattern for $MnCa_2(P_3O_9)_2.10H_2O$ is given in Table 2.

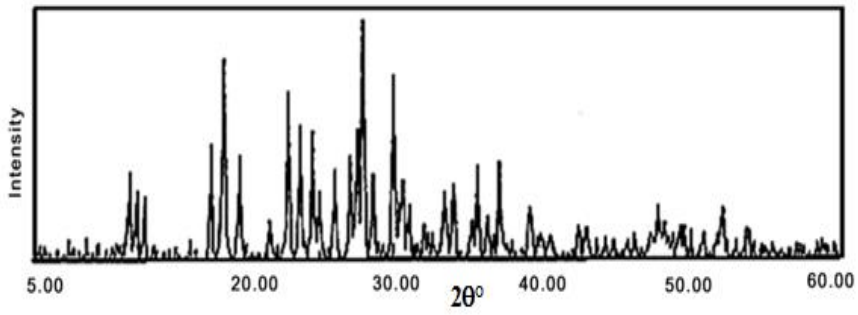

Figure 2. X-ray powder diffraction pattern for $MnCa_2(P_3O_9)_2.10H_2O$.

Table 2. Indexing of the X-ray powder diffraction pattern for $MnCa_2(P_3O_9)_2.10H_2O$.

2θobs (°)	dobs (Å)	100I/I0	hkl	2θcal (°)	dcal(Å)	Δ2θ
6,2997	7,02	37	101	6,2997	7,02	0,0000

2θobs (°)	dobs (Å)	100I/I0	hkl	2θcal (°)	dcal(Å)	Δ2θ
6,3634	6,95	29	1	6,3634	6,95	0,0000
6,6118	6,69	26	111	6,6317	6,67	-0,0199
8,8266	5,02	48	130	8,8266	5,02	0,0000
9,2346	4,8	83	111	9,1386	4,85	0,0960
9,7685	4,54	44	40	9,7903	4,53	-0,0218
10,8022	4,11	17	221	10,8557	4,09	-0,0535
11,4420	3,883	70	41	11,4420	3,883	0,0000
11,8600	3,748	56	2	11,8089	3,764	0,0511
12,2617	3,627	54	122	12,2515	3,63	0,0103
12,4820	3,564	28	202	12,6772	3,51	-0,1952
13,0127	3,421	38	212	12,9626	3,434	0,0501
13,5405	3,29	44	222	13,6206	3,271	-0,0802
13,7926	3,231	55	241	13,8231	3,224	-0,0305
13,9511	3,195	100	32	13,9511	3,195	0,0000
14,3123	3,116	36	311	14,2608	3,127	0,0514
15,0113	2,974	76	231	15,0217	2,972	-0,0103
15,3441	2,911	33	42	15,4037	2,9	-0,0596
15,5410	2,875	23	42	15,4584	2,89	0,0827
6,2997	7,02	37	101	6,2997	7,02	0,0000
6,3634	6,95	29	1	6,3634	6,95	0,0000
6,6118	6,69	26	111	6,6317	6,67	-0,0199
8,8266	5,02	48	130	8,8266	5,02	0,0000
9,2346	4,8	83	111	9,1386	4,85	0,0960
9,7685	4,54	44	40	9,7903	4,53	-0,0218
10,8022	4,11	17	221	10,8557	4,09	-0,0535
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11,8600	3,748	56	2	11,8089	3,764	0,0511
12,2617	3,627	54	122	12,2515	3,63	0,0103
12,4820	3,564	28	202	12,6772	3,51	-0,1952
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13,7926	3,231	55	241	13,8231	3,224	-0,0305
13,9511	3,195	100	32	13,9511	3,195	0,0000
14,3123	3,116	36	311	14,2608	3,127	0,0514
15,0113	2,974	76	231	15,0217	2,972	-0,0103
15,3441	2,911	33	42	15,4037	2,9	-0,0596
15,5410	2,875	23	42	15,4584	2,89	0,0827
6,2997	7,02	37	101	6,2997	7,02	0,0000
6,3634	6,95	29	1	6,3634	6,95	0,0000
6,6118	6,69	26	111	6,6317	6,67	-0,0199
8,8266	5,02	48	130	8,8266	5,02	0,0000
9,2346	4,8	83	111	9,1386	4,85	0,0960
9,7685	4,54	44	40	9,7903	4,53	-0,0218
10,8022	4,11	17	221	10,8557	4,09	-0,0535
11,4420	3,883	70	41	11,4420	3,883	0,0000
11,8600	3,748	56	2	11,8089	3,764	0,0511
12,2617	3,627	54	122	12,2515	3,63	0,0103
12,4820	3,564	28	202	12,6772	3,51	-0,1952
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13,7926	3,231	55	241	13,8231	3,224	-0,0305
13,9511	3,195	100	32	13,9511	3,195	0,0000
14,3123	3,116	36	311	14,2608	3,127	0,0514
15,0113	2,974	76	231	15,0217	2,972	-0,0103
15,3441	2,911	33	42	15,4037	2,9	-0,0596
15,5410	2,875	23	42	15,4584	2,89	0,0827
16,0448	2,787	15	132	16,0863	2,78	-0,0415
16,2849	2,747	11	241	16,4077	2,727	-0,1228
16,6526	2,688	28	330	16,6081	2,695	0,0445
16,9446	2,643	32	44265	16,8985	2,65	0,0461
17,5824	2,55	17	44276	17,5610	2,553	0,0213
17,7622	2,525	39	301	17,7549	2,526	0,0073
18,1031	2,479	18	44277	18,0956	2,48	0,0076

2θobs (°)	dobs (Å)	100I/I0	hkl	2θcal (°)	dcal(Å)	Δ2θ
18,5049	2,427	41	44268	18,5049	2,427	0,0000
21,1593	2,134	14	72	21,1593	2,134	0,0000
21,4545	2,106	13	44280	21,4973	2,102	-0,0429
23,8507	1,905	22	153	23,8640	1,904	-0,0133
24,0925	1,887	15	31-4	24,0925	1,887	0,0000
24,7630	1,839	14	182	24,8062	1,836	-0,0432
24,9806	1,824	12	441	24,9806	1,824	0,0000
25,3823	1,797	11	510	25,3823	1,797	0,0000
25,9869	1,758	22	47-1	26,0187	1,756	-0,0318
26,7904	1,709	13	402	26,8243	1,707	-0,0339
26,8924	1,703	12	124	26,8924	1,703	0,0000
16,0448	2,787	15	132	16,0863	2,78	-0,0415
16,2849	2,747	11	241	16,4077	2,727	-0,1228
16,6526	2,688	28	330	16,6081	2,695	0,0445
16,9446	2,643	32	44265	16,8985	2,65	0,0461
17,5824	2,55	17	44276	17,5610	2,553	0,0213
17,7622	2,525	39	301	17,7549	2,526	0,0073
18,1031	2,479	18	44277	18,0956	2,48	0,0076
18,5049	2,427	41	44268	18,5049	2,427	0,0000
21,1593	2,134	14	72	21,1593	2,134	0,0000
21,4545	2,106	13	44280	21,4973	2,102	-0,0429
23,8507	1,905	22	153	23,8640	1,904	-0,0133
24,0925	1,887	15	31-4	24,0925	1,887	0,0000
24,7630	1,839	14	182	24,8062	1,836	-0,0432
24,9806	1,824	12	441	24,9806	1,824	0,0000
25,3823	1,797	11	510	25,3823	1,797	0,0000
25,9869	1,758	22	47-1	26,0187	1,756	-0,0318
26,7904	1,709	13	402	26,8243	1,707	-0,0339
26,8924	1,703	12	124	26,8924	1,703	0,0000
16,0448	2,787	15	132	16,0863	2,78	-0,0415
16,2849	2,747	11	241	16,4077	2,727	-0,1228
16,6526	2,688	28	330	16,6081	2,695	0,0445
16,9446	2,643	32	44265	16,8985	2,65	0,0461
17,5824	2,55	17	44276	17,5610	2,553	0,0213
17,7622	2,525	39	301	17,7549	2,526	0,0073
18,1031	2,479	18	44277	18,0956	2,48	0,0076
18,5049	2,427	41	44268	18,5049	2,427	0,0000
21,1593	2,134	14	72	21,1593	2,134	0,0000
21,4545	2,106	13	44280	21,4973	2,102	-0,0429
23,8507	1,905	22	153	23,8640	1,904	-0,0133
24,0925	1,887	15	31-4	24,0925	1,887	0,0000
24,7630	1,839	14	182	24,8062	1,836	-0,0432
24,9806	1,824	12	441	24,9806	1,824	0,0000
25,3823	1,797	11	510	25,3823	1,797	0,0000
25,9869	1,758	22	47-1	26,0187	1,756	-0,0318
26,7904	1,709	13	402	26,8243	1,707	-0,0339
26,8924	1,703	12	124	26,8924	1,703	0,0000

3.3. $MnCa_2(P_3O_9)_2$.

$MnCa_2(P_3O_9)_2$ is isotype to $M^{II}Tl_4(P_3O_9)_2$ (M^{II} = Ca, Mg) [27] and crystallizes in the hexagonal system, Z = 2, and the space group is P3. The unit-cell parameters are a = b = 7.392 Å (9) and c = 20.134 (2) Å. This isotopy can be explained by the substitution of two cations of the structure of $CaTl_4(P_3O_9)_2$ or $MgTl_4(P_3O_9)_2$ by a cation M^{II} of $MnCa_2(P_3O_9)_2$, which respects electroneutrality with half of the unoccupied sites.

$M^{II}M^{I}_4(P_3O_9)_2$ <=> $M'^{II}\ M''^{II}_2(P_3O_9)_2$

M^{II} <=> M'^{II}

$4M^{I}$ <=> $2M'^{II}$

$2M^{I}$ <=> M'^{II}

The X-ray powder diffraction pattern for *$MnCa_2(P_3O_9)_2$* is reported in Figure 3. Indexing of the X-ray powder diffraction pattern for *$MnCa_2(P_3O_9)_2$* is given in Table 3.

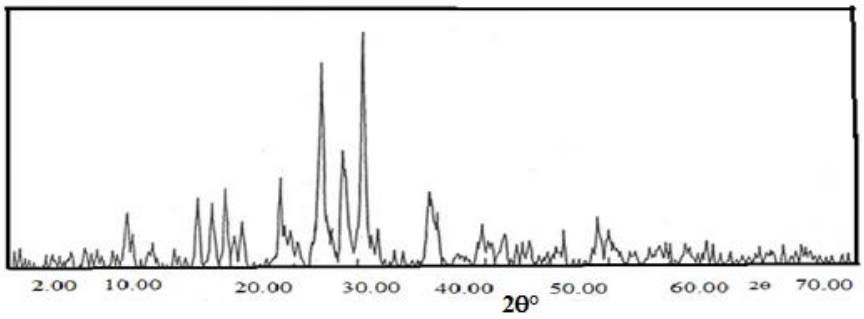

Figure 3. X-ray powder diffraction pattern for $MnCa_2(P_3O_9)_2$.

Table 3. Indexing of the X-ray powder diffraction pattern for $MnCa_2(P_3O_9)_2$.

2θobs (°)	dobs (Å)	100I/I0	hkl	2θcal (°)	dcal(Å)	Δ2θ
6,9128	6,4	11	100	6,9128	6,4	0,0000
17,8719	2,51	32	025	17,8499	2,513	0,0221
8,7738	5,05	30	004	8,7563	5,06	0,0175
18,0429	2,487	23	116	18,1714	2,47	-0,1285
9,5560	4,64	28	103	9,5146	4,66	0,0414
12,0162	3,7	38	011	11,9702	3,714	0,0460
12,8258	3,47	11	112	12,6772	3,51	0,1486
19,8638	2,267	18	213	19,9004	2,263	-0,0366
13,2411	3,363	11	006	13,2411	3,363	0,0000
20,6723	2,182	10	214	20,2741	2,223	0,3982
13,8362	3,221	87	200	13,6037	3,275	0,2326
20,6921	2,18	14	214	20,7919	2,17	-0,0998
14,1043	3,161	10	201	14,0318	3,177	0,0725
21,6487	2,088	10	302	21,6270	2,09	0,0218
14,6239	3,051	35	202	14,5799	3,06	0,0440
21,7913	2,075	11	215	21,8023	2,074	-0,0110
23,0919	1,964	15	304	23,1793	1,957	-0,0874
14,9958	2,977	100	16	15,1891	2,94	-0,1932
24,5635	1,853	21	217	24,5353	1,855	0,0282
15,4584	2,89	14	203	15,5521	2,873	-0,0938
24,8062	1,836	15	209	25,0392	1,82	-0,2330

2 Theta range: 2-70° (2θ), Step size: 0.01° (2θ), Counting time: 30 s

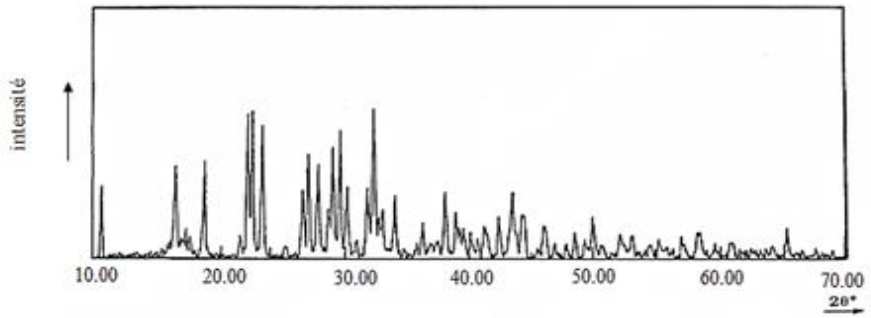

Figure 4. X-ray powder diffraction pattern for $MnBa_2(P_3O_9)_2.6H_2O$.

3.4. $MnBa_2(P_3O_9)_2.6H_2O$.

The cyclotriphosphate hexahydrate of manganese and barium, $MnBa_2(P_3O_9)_2.6H_2O$ [28],is isotype to $Ba_3(P_3O_9)_2.6H_2O$ [29], and crystallizes in the triclinic system, Z =2 and the space group is P-1. The unit-cell parameters, calculated by the Weisenberg method and refined

by the least squares method are: a = 7,479 (6)Å, b = 11,942 (8)Å, c = 12,786 (9)Å, α=105,94(7)°, β=98,40°(7), γ = 98,16 (7)° and V = 1046,8 (2) $Å^3$ [30].

The X-ray powder diffraction pattern for $MnBa_2(P_3O_9)_2 \cdot 6H_2O$ is reported in Figure 4. Indexing of the X-ray powder diffraction pattern for $MnBa_2(P_3O_9)_2.6H_2O$ is given in Table 4.

Table 4. Indexing of the X-ray powder diffraction pattern for $MnBa_2(P_3O_9)_2.6H_2O$.

2θobs (°)	dobs (Å)	100I/I0	hkl	2θcal (°)	dcal(Å)	Δ2θ
7,9924	5,54	13	020	7,9635	5,56	0,0289
18,1638	2,471	24	140	18,1638	2,471	0,0000
8,3095	5,33	61	10-2	8,2627	5,36	0,0468
18,4262	2,437	24	-13-1	18,4262	2,437	0,0000
8,7043	5,09	13	11-2	8,7043	5,09	0,0000
18,7532	2,396	12	14-4	18,7532	2,396	0,0000
8,8266	5,02	10	012	8,8981	4,98	-0,0715
19,0251	2,363	44	31-2	19,0502	2,36	-0,0251
10,8557	4,09	13	11-3	10,8557	4,09	0,0000
19,4965	2,308	31	05-1	19,4965	2,308	0,0000
10,9642	4,05	96	-103	11,1312	3,99	-0,1670
19,6115	2,295	18	05-3	19,6293	2,293	-0,0178
11,4152	3,892	98	03-1	11,3005	3,931	0,1148
19,8183	2,272	15	-32-2	19,8183	2,272	0,0000
11,7645	3,778	88	03-2	11,7111	3,795	0,0534
20,0296	2,249	18	-313	20,0948	2,242	-0,0652
12,5680	3,54	13	-130	12,5933	3,533	-0,0253
20,3890	2,211	13	006	20,3698	2,213	0,0192
13,3016	3,348	46	-220	13,3299	3,341	-0,0284
20,6723	2,182	22	24-2	20,6426	2,185	0,0297
13,5615	3,285	69	-212	13,5615	3,285	0,0000
21,1490	2,135	28	-304	21,2010	2,13	-0,0520
13,9556	3,194	63	-221	13,9511	3,195	0,0045
21,8023	2,074	44	24-4	21,7692	2,077	0,0331
14,3782	3,102	33	122	14,3735	3,103	0,0047
21,9806	2,058	14	-116	21,9358	2,062	0,0449
14,5508	3,066	74	20-3	14,5508	3,066	0,0000
22,1391	2,044	29	-10-6	22,1391	2,044	0,0000
14,8226	3,011	85	-12-4	14,8428	3,007	-0,0202
22,2192	2,037	28	150	22,2307	2,036	-0,0115
15,0892	2,959	48	22-2	15,1206	2,953	-0,0314
23,0299	1,969	22	-243	23,0299	1,969	0,0000
15,4638	2,889	15	-213	15,4638	2,889	0,0000
24,2704	1,874	17	-21-6	24,3118	1,871	-0,0414
15,9100	2,81	47	-14-2	15,9041	2,811	0,0058
24,6771	1,845	13	-15-6	24,7200	1,842	-0,0429
16,1639	2,767	100	-13-4	16,1639	2,767	0,0000
25,0099	1,822	28	34-4	25,0246	1,821	-0,0147
16,3154	2,742	13	-140	16,2971	2,745	0,0183
26,0506	1,754	16	06-1	26,0506	1,754	0,0000
16,5261	2,708	32	11-5	16,5261	2,708	0,0000
26,5722	1,722	15	42-1	26,5889	1,721	-0,0167
16,9843	2,637	42	123	17,0243	2,631	-0,0399
27,6296	1,661	13	-127	27,6477	1,66	-0,0181
17,3783	2,579	15	03-5	17,4062	2,575	-0,0279
29,2391	1,577	17	136	29,2391	1,577	0,0000
17,9607	2,498	15	-311	17,9607	2,498	0,0000

2 Theta range:10-70°(2θ), Step size: 0.01°(2θ), Counting time: 30 s

Conclusions

In the present work, we investigate crystallographic characterization for a series of cyclotriphosphates type $MnM^{II}_2(P_3O_9)_2.nH_2O$ (M^{II} = Ca, n = 10 et 0; M^{II} = Sr, n = 4 et M^{II} = Ba, n = 6) using X-ray powder diffraction patterns. The experimental results are given below - The four cyclotriphosphates $MnCa_2(P_3O_9)_2.10H_2O$, $MnCa_2(P_3O_9)_2$, $MnSr_2(P_3O_9)_2.4H_2O$ and

$MnBa_2(P_3O_9)_2.6H_2O$ were prepared in three different ways, the method of ion-exchange resin for $MnSr_2(P_3O_9)_2.4H_2O$ and $MnBa_2(P_3O_9)_2.6H_2O$, by nitrates for $MnCa_2(P_3O_9)_2.10H_2O$ and by total thermal dehydration for $MnCa_2(P_3O_9)_2$. Till now, there is only one cyclotriphosphate having the same formula $ZnBa_2(P_3O_9)_2.10H_2O$ whose structure is known. The four cyclotriphosphates are not isotypic even they have the same formula containing manganous cation associated respectively to alkaline earth s Ba, Ca, and Sr. $MnSr_2(P_3O_9)_2.4H_2O$ and $MnBa_2(P_3O_9)_2.6H_2O$ crystallize in the triclinic system, $MnCa_2(P_3O_9)_2.10H_2O$ has a monoclinic structure, and $MnCa_2(P_3O_9)_2$ has a hexagonal symmetry. It is worth noticing that the structure of the cyclotriphosphate $MnSr_2(P_3O_9)_2.4H_2O$ is unknown. The total thermal dehydration of the series of cyclotriphosphates type $MnM^{II}_2(P_3O_9)_2.nH_2O$ (M^{II} = Ca, n = 10 et 0; M^{II} = Sr, n = 4 et M^{II} = Ba, n = 6) leads to the anhydrous form only for $MnCa_2(P_3O_9)_2$.

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Conflicts of Interest

The authors declare no conflict of interest.

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