

CHEMICAL PREPARATION, CRYSTALLOGRAPHIC CHARACTERIZATION AND VIBRATIONAL STUDY OF TWO NEW CONDENSED PHOSPHATES

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Abstract

Chemical preparation, crystallographic characterization and vibrational studies are reported for two new condensed phosphates associated to nickel-rubidium $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$ and strontium-thallium $\text{SrTl}_4(\text{P}_3\text{O}_9)_2$. $\text{SrTl}_4(\text{P}_3\text{O}_9)_2$ was prepared by the method of ion-exchange resin and $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$ was obtained by total thermal dehydration of $\text{NiRb}_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$. $\text{SrTl}_4(\text{P}_3\text{O}_9)_2$ is rhombohedral, $Z = 2$, space group $P\bar{3}1c$, with the following unit-cell parameters: $a = 7,424(1) \text{ \AA}$, $c = 20,176(2) \text{ \AA}$ and $V = 2807.46(2) \text{ (\AA}^3\text{)}$. $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$ is triclinic, $Z = 2$, space group $P\bar{1}$, with the following unit-cell parameters: $a = 8,046(9) \text{ \AA}$, $b = 9,733(0) \text{ \AA}$, $c = 4,327(5) \text{ \AA}$, $\alpha = 98.053^\circ$, $\beta = 88.616^\circ$, $\gamma = 84.761^\circ$ and $V = 333,95(2) \text{ (\AA}^3\text{)}$. Vibrational study is also reported for the title compounds.

Keywords: Chemical preparation, crystallographic characterization, infrared spectrometry, $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$, $\text{SrTl}_4(\text{P}_3\text{O}_9)_2$.

1- INTRODUCTION

During a systematic investigation of cyclotriphosphates type $\text{M}^{\text{II}}\text{M}^{\text{I}}_4(\text{P}_3\text{O}_9)_2 \cdot n\text{H}_2\text{O}$ ($\text{M}^{\text{II}} = \text{Ni, Mn, Ca, Ba, Sr}$ and $\text{M}^{\text{I}} = \text{Li, Na, K, Cs, Rb, Tl, NH}_4$), two new cyclotriphosphates were prepared by two different methods. The total thermal dehydration of cyclotriphosphate hexahydrate associated to nickel and rubidium, $\text{NiRb}_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$ [1], leads to the corresponding anhydrous new form $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$ [2]. The cyclotriphosphate associated to strontium and thallium, $\text{SrTl}_4(\text{P}_3\text{O}_9)_2$, was prepared during the elaboration of condensed phosphates $\text{SrM}^{\text{I}}_4(\text{P}_3\text{O}_9)_2 \cdot n\text{H}_2\text{O}$ ($\text{M}^{\text{I}} = \text{Li, Na, K, Cs, Rb, Tl, NH}_4$) by the method of ion-exchange resin. This study reports the chemical preparation, XRD data and IR studies for two new cyclotriphosphates $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$ and $\text{SrTl}_4(\text{P}_3\text{O}_9)_2$. The two condensed phosphates are stable in the normal conditions of temperature and hygrometry.

2- MATERIAL AND METHODS

2.2. Experimental

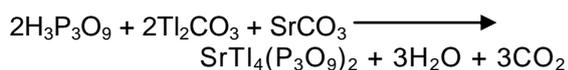
X-ray diffraction. Powder diffraction patterns for the two title compounds were collected with a SIEMENS D 5000 diffractometer using $\text{Cu } K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). The experimental 2θ range was from 5 to 60° (2θ) with a step size of 0.017° and a counting time of 160.9603s per step. The program of graphic tool for powder diffraction named WinPLOTR (January 2012) was used to determine the observed diffraction peak positions for $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$ and $\text{SrTl}_4(\text{P}_3\text{O}_9)_2$. The unit-cell parameters were calculated by means of the computer program Mc Maille [3].

Infrared spectrometry. Spectra were recorded in the range $4000\text{-}400 \text{ cm}^{-1}$ with a Perkin-Elmer IR 983G spectrophotometer, using samples dispersed in spectroscopically pure KBr pellets.

2.2. Synthesis

2.2.1. SrTi₄(P₃O₉)₂

Polycrystalline samples of SrTi₄(P₃O₉)₂ were prepared by slowly adding dilute cyclotriphosphoric acid, H₃P₃O₉, to an aqueous solution of strontium carbonate and thallium carbonate, Tl₂CO₃ and SrCO₃, according to the following chemical reaction :



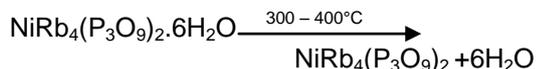
The so-obtained solution was then slowly evaporated at room temperature until polycrystalline samples of SrTi₄(P₃O₉)₂

were obtained. The cyclotriphosphoric acid, H₃P₃O₉, used in this reaction was prepared from an aqueous solution of Na₃P₃O₉ passed through an ion-exchange resin 'Amberlite IR120' [4].

SrTi₄(P₃O₉)₂ is stable in the normal conditions of temperature and hygrometry. With further increase in temperature, SrTi₄(P₃O₉)₂ is stable until its melting point at 700°C.

2.2.2. NiRb₄(P₃O₉)₂

The product resulting from the total thermal dehydration of NiRb₄(P₃O₉)₂.6H₂O, between 300°C and 400°C, is a ring phosphate [2]. The reaction is the following:



NiRb₄(P₃O₉)₂ is stable in the normal conditions of temperature and hygrometry. With further increase in temperature at 500°C, NiRb₄(P₃O₉)₂ is decomposed into a mixture of long-chain polyphosphates NiRb₂(PO₃)₄ [5] and RbPO₃.

3. RESULTS

3.1. Crystallographic characterization

3.1.1. SrTi₄(P₃O₉)₂

SrTi₄(P₃O₉)₂ has a powder diffraction pattern plotted in Fig. A.1 comparable to MgTi₄(P₃O₉)₂. SrTi₄(P₃O₉)₂ has a rhombohedral symmetry, space group P-3₁c

and Z = 2. The lattice parameters calculated by isotopy with MgTi₄(P₃O₉) [7] are : a = 7,424(1) Å and c = 20,176(2) Å. SrTi₄(P₃O₉)₂ is isotopic to thallium cyclotriphosphates associated to bivalent cations M^{II}Tl₄(P₃O₉)₂ with M^{II} = Ca, Cd,

Co, Mg, Mn, Ni and Zn [8]. SrTi₄(P₃O₉)₂ is also isotopic to M^{II}K₄(P₃O₉)₂ (M^{II} = Co²⁺ and Mn²⁺) [9]. The powder diffraction data of SrTi₄(P₃O₉)₂ are reported in Table A.1.

Table A.1: Powder diffraction data of SrTi₄(P₃O₉)₂.

<i>hkl</i>	<i>d</i> _{obs}	<i>d</i> _{cal}	<i>I</i> _{obs}	<i>hkl</i>	<i>d</i> _{obs}	<i>d</i> _{cal}	<i>I</i> _{obs}
0 0 2	10,09	10,09	8	0 2 6	2,323	2,324	4
1 0 0	6,44	6,43	4	1 2 3	2,286	2,286	2
1 0 1	6,13	6,13	8	3 0 0	2,143	2,143	40
0 0 4	5,05	5,04	12	1 0 9	2,117	2,117	7
1 0 3	4,65	4,65	2	1 2 -5	2,082	2,082	15
0 1 4	3,968	3,969	4	2 0 8	1,985	1,984	3
1 1 0	3,710	3,712	100	0 3 4	1,972	1,973	19
1 1 2	3,482	3,484	22	1 0 10	1,925	1,925	4
0 1 5	3,416	3,418	47	2 2 0	1,856	1,856	11
2 0 1	3,175	3,175	20	0 2 9	1,839	1,839	6
1 1 4	2,988	2,990	73	2 2 2	1,824	1,825	3
0 2 3	2,899	2,900	3	3 1 1	1,775	1,776	3
0 1 7	2,630	2,630	4	2 2 4	1,742	1,742	13
2 0 5	2,515	2,514	16	0 2 10	1,709	1,709	2
2 1 1	2,412	2,413	17	2 1 9	1,647	1,648	8

3.1.2. NiRb₄(P₃O₉)₂

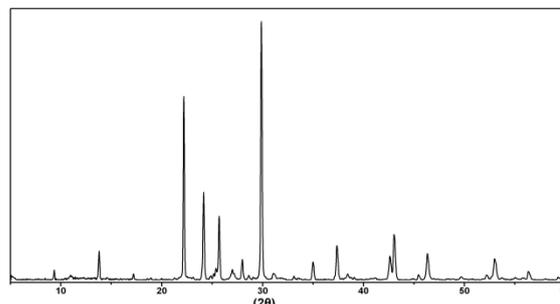


Fig. 2.A. X-ray powder diffraction patterns for NiRb₄(P₃O₉)₂

NiRb₄(P₃O₉)₂ is triclinic, Z = 2, space group P-1, with the following unit-cell parameters :

a = 8,046(9) Å, b = 9,733(0) Å, c = 4,327(5) Å, α = 98.053 °, β = 88.616° and γ = 84.761°. The powder diffraction pattern of NiRb₄(P₃O₉)₂ is plotted in Fig. A.2 and the powder diffraction data of NiRb₄(P₃O₉)₂ are reported in Table A.2.

Table A.2: Powder diffraction data of NiRb₄(P₃O₉)₂.

<i>hkl</i>	<i>d</i> _{obs}	<i>d</i> _{cal}	<i>I</i> _{obs}	<i>hkl</i>	<i>d</i> _{obs}	<i>d</i> _{cal}	<i>I</i> _{obs}
0 1 0	9,45	9,59	12	0 2 1	2,989	2,989	100
1 1 0	6,42	6,46	18	1 -3 1	2,562	2,562	9
2 0 0	4,00	4,00	72	0 3 1	2,405	2,403	15
1 1 -1	3,682	3,683	37	1 -4 1	2,120	2,113	11
1 1 1	3,465	3,465	27	3 -1 -1	2,100	2,100	19
1 -1 -1	3,299	3,286	8	3 -3 0	1,958	1,959	12
0 3 0	3,186	3,198	12	0 4 -2	1,727	1,724	10

3.2. Vibrational Study

3.2.1. Characterization of SrTi₄(P₃O₉)₂ by IR vibration spectrometry

SrTi₄(P₃O₉)₂ has a rhombohedral symmetry, space group P-3₁c and Z = 2. The range 1400-650 cm⁻¹, characteristic of the valence vibration bands of the cycle [2, 10, 11], will be examined on the basis, of our results of the 30 normal calculated frequencies of the P₃O₉ ring with high symmetry D_{3h}, of the frequency shifts during theoretical and successive isotopic substitutions of the equivalent atoms ³¹P-³³P, ¹⁶O_i-¹⁸O_i and ¹⁶O_e-¹⁸O_e, of the three equivalent atoms (3P,3O_i and 6O_e) belonging to the P₃O₉ ring (D_{3h}). The reduced

$\Gamma_{int} = 4A'_1(-,Ra) + 2A'_2(-,-) + 6E'(IR,Ra) + A''_1(-,-) + 3A''_2(IR,-) + 4E''(-,Ra)$. The cycle P₃O₉ is built, theoretically, by three external (PO₂) groups and the P₃O₃ ring. Theoretical group analysis leads, for the valence vibration bands (the only ones which we consider here) to $\Gamma_{PO_2} = A'_1(-,Ra) + A'_2(IR,-) + E'(IR,Ra) + E''(-,Ra)$ and $\Gamma_{P_3O_3} = A'_1(-,Ra) + A'_2(-,-) + 2E'(IR,Ra)$. Theoretical group analysis predicts six valence vibration bands for the PO₂ groups, six valence vibration bands for the P₃O₃ ring and 18 bending vibration bands for the P₃O₉ ring, $\Gamma_{bending} = 2A'_1(-,Ra) + A'_2(-,-) + A''_1(-,-) + 2A''_2(IR,-) + 3E'(IR,Ra) + 3E''(-,Ra)$. These thirty fundamental frequencies of the cycle, D_{3h}, were calculated, by the MNDO method [12], and their attribution was made by using

Table 3: IR frequencies and displacements ($\Delta\nu$ in cm⁻¹) calculated for the D_{3h} symmetry and for the substitutions of the internal oxygen atoms (Oi), of the external oxygen atoms (Oe) by the isotope ¹⁸O and of the phosphorus atoms by the isotope ³³P and percentage of participation of the POP and PO₂ groups

³¹ P ₃ ¹⁶ O ₉ ³⁻			³¹ P ₃ ¹⁸ O ₃ ¹⁶ O ₆ ³⁻		³³ P ₃ ¹⁶ O ₉ ³⁻		³¹ P ₃ ¹⁶ O ₃ ¹⁸ O ₆ ³⁻		% of Participation
$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	
1288.39	1287.80	0.59	1269.56	18.83	1249.94	38.45			v _{as} PO ₂ [99]
1272.42	1272.03	0.39	1254.33	18.09	1233.29	39.13			
1272.42	1272.03	0.39	1254.33	18.09	1233.29	39.13			v _{as} PO ₂ [100]
1225.23	1179.02	46.20	1215.36	9.87	1223.90	1.32			
1225.23	1179.02	46.20	1215.36	9.87	1223.90	1.32			v _{as} POP [98] + v _s PO ₂ [2]
1169.25	1168.86	0.39	1156.27	12.98	1127.60	41.65			
1108.62	1098.55	10.07	1102.24	6.38	1062.88	45.74			v _s PO ₂ [100]
1108.62	1098.55	10.07	1102.24	6.38	1062.88	45.74			
1059.41	1010.98	48.43	1053.00	6.41	1058.95	0.46			v _{as} POP [18] + v _s PO ₂ [82]
780.72	768.35	12.36	765.35	15.37	775.94	4.78			
780.72	768.35	12.36	765.35	15.37	775.94	4.78			v _{as} POP [100]
671.06	659.43	11.64	663.25	7.82	660.26	10.81			
559.30	537.04	22.26	555.32	3.98	552.99	6.31			v _s POP [73] + δ PO ₂ [27]
511.49	496.11	15.38	509.22	2.27	501.42	10.07			
436.79	433.11	3.68	432.47	4.32	422.93	13.86			v _s POP [52] + δ PO ₂ [48]
436.79	433.11	3.68	432.47	4.32	422.93	13.86			
420.11	417.43	2.68	416.98	3.13	411.08	9.03			γ POP [60] + γ_R PO ₂ [40]
418.64	406.27	12.37	416.98	1.66	410.11	8.52			
418.64	406.27	12.37	413.15	5.49	410.11	8.52			δ POP _{cyc} [78] + δ PO ₂ [22]
302.05	301.64	0.41	301.40	0.64	289.37	12.68			
298.72	292.60	6.12	298.18	0.54	289.37	9.35			δ POP [21] + δ PO ₂ [79]
298.72	292.60	6.12	298.18	0.54	285.93	12.79			
280.98	279.09	1.89	279.07	1.91	269.75	11.23			γ_w PO ₂ [78]
280.98	279.09	1.89	279.07	1.91	269.75	11.23			
256.58	253.04	3.55	255.07	1.51	246.51	10.07			γ POP [59] + γ_T PO ₂ [41]
256.58	253.04	3.55	255.07	1.51	246.51	10.07			
214.09	214.06	0.03	214.06	0.03	201.82	12.28			δ PO ₂ [98]
49.31	48.52	0.79	49.29	0.02	47.21	2.10			
35.02	34.37	0.65	35.02	0.00	33.59	1.43			δ POP[40] + γ_w PO ₂ [60]
35.02	34.37	0.65	35.02	0.00	33.59	1.43			

v_{as} : asymmetric stretching; v_s : symmetric stretching; δ : bending; γ : out of plane P₃O₃; γ_w : wagging ($\gamma \perp \text{PO}_2$); γ_R : rocking ($\gamma // \text{PO}_2$); γ_T : twisting; O_i : internal oxygen atom of the ring and O_e: external oxygen atom of the ring

representation of the internal modes of the isolated ring P₃O₉ with D_{3h} symmetry is

successive isotopic substitutions ¹⁶O_i-¹⁸O_i, ³¹P-³³P and ¹⁶O_e-¹⁸O_e (Table A.3). From the

isotopic effects ($\Delta\nu$), the contribution of each group of atoms, POiP and/or PO₂, to each calculated normal frequency was determined. With this intention, we supposed that the pure movements of the POiP groups must leave the external oxygen atoms, O_e, fixed and those due to 100% of internal groups, O_i, fixed. By means of this assumption, the percentage of participation of each group was determined (Table A.3). We notice that the calculated frequencies values for the D_{3h} symmetry, are similar to those observed in the IR spectrum of SrTi₄(P₃O₉)₂.

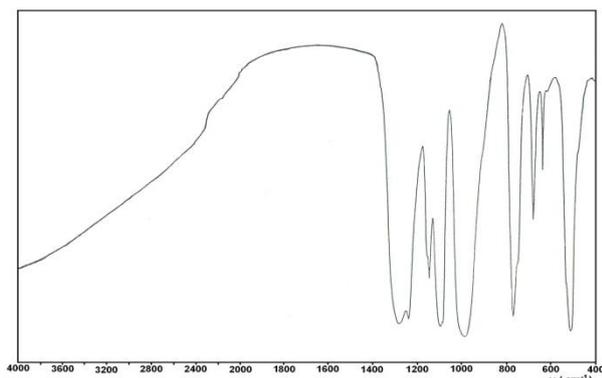


Fig. 3.A. - IR absorption spectrum of SrTi₄(P₃O₉)₂

The crystalline structure of MgTi₄(P₃O₉)₂ [7], proposed for srTi₄(P₃O₉)₂ new phase, is described in the space group P-3₁c (D_{3d}²) with two formula units (Z = 2) per unit-cell. The crystalline unit-cell contains four

cycles occupying sites with local symmetry C₃. During the passage from the symmetry D_{3h} to the C₃ symmetry of the cycle, supposed isolated, of SrTi₄(P₃O₉)₂, the simple normal modes A¹, A², A¹₁ and A²₂, of the symmetry D_{3h}, are resolved each one into the mode A, of the symmetry C₃, and the doubly degenerate E¹ and E² modes are resolved into the mode E of the symmetry C₃. For this reason, 8 IR bands are predicted, in the range of valence vibrations, for the isolated cycle with symmetry C₃ which has four vibration frequencies with simple modes A and four modes E. The experimental IR spectrum of SrTi₄(P₃O₉)₂ (Fig. A.3) shows, in the domain 1400-650 cm⁻¹, 6 IR fundamental bands. This number of six bands is less than that predicted for an isolated cycle with symmetry C₃. When we pass from the isolated cycle with symmetry C₃ to the crystalline unit-cell of SrTi₄(P₃O₉)₂ containing 4 cycles in interaction between them, the four IR bands with modes E, of the C₃ symmetry, should appear in the shape of a doublet of frequencies with modes E_u of the group factor D_{3d}. This situation is due to the correlation group C₃ – group factor D_{3d} resolving the mode A, of C₃, into modes A_{1g}(-, Ra) + A_{2g}(-, -) + A_{1u}(-, -) + A_{2u}(IR, Ra), of the group D_{3d}, and the mode E into 2E_g(-, Ra) + 2E_u(IR, -). On the basis of our results of calculations of the normal frequencies of the P₃O₉³⁻ cycle with high symmetry D_{3h} and the correlations group D_{3h} – groups with low symmetries C₃ and C₁, the assignment of the valence frequencies of the cycle, is given in Table A.4.

Table 4 Attribution of the observed valence IR frequencies (cm⁻¹) of the P₃O₉ ring (C₃) in SrTi₄(P₃O₉)₂

S. G.		$\Delta\nu$ (cm ⁻¹)			SrTi ₄ (P ₃ O ₉) ₂		
C ₃ vcal (cm ⁻¹)	I/Imax	Mode (IR, Ra)	¹⁶ O _i - ¹⁸ O _i	³¹ P- ³³ P	¹⁶ O _e - ¹⁸ O _e	IR	Main Movement
1288.39	55.20	A (+,+)	0.59	18.83	38.45	1286	v _{as} PO ₂
1272.42	0.01	E (+,+)	0.39	18.09	39.13	1234	v _{as} PO ₂
1272.42	0.01	E (+,+)	0.39	18.09	39.13		
1225.23	100.00	E (+,+)	46.20	9.87	1.32		v _{as} POP
1225.23	100.00		46.20	9.87	1.32		
1169.25	0.00	A (+,+)	0.39	12.98	41.65	1153 1096	v _s PO ₂
1108.62	5.81	E (+,+)	10.07	6.38	45.74	1084	v _s PO ₂
1108.62	5.81		10.07	6.38	45.74		
1059.41	0.00	A (+,+)	48.43	6.41	0.46	986	v _{as} POP combination
780.72	18.34	E (+,+)	12.36	15.37	4.78	774	v _s POP
780.72	18.34		12.36	15.37	4.78		
671.06	0.01	A (+,+)	11.64	7.82	10.67	680	v _s POP

$\Delta\nu$ (cm⁻¹) effect of the isotopic substitution; $\Delta\nu$ (cm⁻¹) : difference between the calculated value of the frequency before and after the substitution; S. G. : site group.

3.2.2. Characterization of NiRb₄(P₃O₉)₂ by IR vibration spectrometry

The IR absorption spectrum of NiRb₄(P₃O₉)₂ is reported in Fig. A.4.

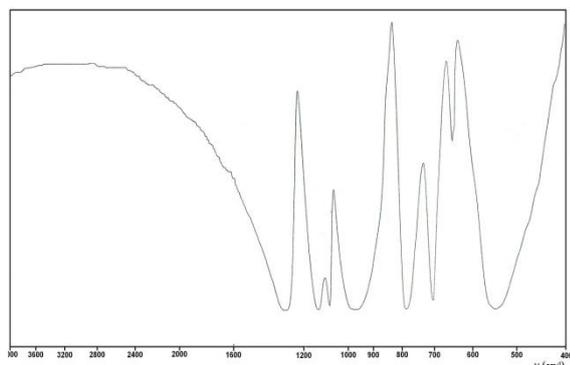


Fig. 4.A. - IR absorption spectrum of NiRb₄(P₃O₉)₂

Between 1340 and 660 cm⁻¹ the spectrum (a) (Fig. A.4) shows valency vibration bands characteristic of phosphates with ring anions P₃O₉³⁻ [13-16]. Among these bands can be distinguished :

- the vibration bands of the (OPO) end groups at high frequencies : 1180 < ν_{as} OPO < 1340 cm⁻¹ and 1060 < ν_s OPO < 1180 cm⁻¹ ;
- the valency vibrations of the (P-O-P) ring groups at : 960 < ν_{as} POP < 1060 cm⁻¹ and 660 < ν_s POP < 960 cm⁻¹ ;

The valency vibrations of the (POP) ring groups are represented in the spectrum (a) (Fig. A.4) by a very strong band at about 983 cm⁻¹ which can be attributed to the ν_{as} POP antisymmetric vibrations and by a strong band between 700 and 800 cm⁻¹ (at 744 cm⁻¹) which can be related to the ν_s POP symmetric vibrations. The strong band at 744 cm⁻¹ characterize with no ambiguity the structure of a cyclotriphosphate P₃O₉³⁻ [13].

Between 660 and 400 cm⁻¹ the spectrum (a) (Fig. A.4) shows bending vibration bands characteristic of phosphates with ring anions [13-16]. The nature of the vibration corresponding to the different observed bands is given in Table A.5.

Table 5. Frequencies (cm⁻¹) of IR absorption bands for NiRb₄(P₃O₉)₂

ν (cm ⁻¹)	Vibration
1293	ν_{as} OPO ⁻
1130	ν_s OPO ⁻
1075	
971	ν_{as} POP
782	ν_s POP
700	
643	δ OPO ⁻ + ρ OPO
540	

3.2.3. Interpretation of the infrared (IR) spectrum of NiRb₄(P₃O₉)₂ and vibrations analysis of the four cycles P₃O₉³⁻ contained in the cyclotriphosphate, NiRb₄(P₃O₉)₂

NiRb₄(P₃O₉)₂ is triclinic P-1 (C_i) with two formula units Z = 2. The four cycles P₃O₉³⁻ of the unit-cell occupy each one a site with symmetry C₁, and two cycles can be deduced from the two others by symmetry center i.

The local symmetry C₁ in the isolated cycle P₃O₉³⁻ of NiRb₄(P₃O₉)₂ is the same as that found by SBAI et al. [9, 16], TRIDANE [17], BELAAOUAD et al. [18, 19] and KHEIREDDINE et al. [20, 21] in other cyclotriphosphates. This leads at the level of the isolated cycle P₃O₉³⁻ with C_{3v} symmetry to the same selection rules and to the same description of the vibrations (Table A.6).

Theoretical group analysis leads to the following correlation diagram:

The reduced representation of the internal modes of the four cycles P₃O₉³⁻ of the unit-cell is: $\Gamma = 60 A_g + 60 A_u$, this means 60 modes active in IR (60 A_u) and the same number 60 modes active in Raman (60 A_g). The table 7 gives the representation and the separation of the internal modes into stretching and bending modes.

It comes out from this theoretical analysis of the vibrations that when we pass from the isolated cycle with local symmetry C₁ to the unit-cell of NiRb₄(P₃O₉)₂ the number of the stretching vibrations active in IR (or in Raman) must pass from 12 to 24. If all the couplings are possible, the number of the stretching vibrations of the isolated cycle C_{3v} must pass from 7 to 24. Each frequency corresponding to a simple mode A, (of the C_{3v} cycle) must appear in the form of a doublet of frequencies and each frequency corresponding to a doubly degenerated mode must appear in the form of a quadruplet. These frequencies must be distributed, in the form of 6 frequencies, in each of the four ranges of the stretching vibrations ν_{as} O-P-O⁻, ν_s O-P-O⁻, ν_{as} P-O-P et ν_s P-O-P. The IR spectrum of NiRb₄(P₃O₉)₂ does'nt express any index of vibrational coupling, of the cycles of the unit-cell , because the number of the frequencies observed in each of the four ranges, mentioned above, of the stretching vibrations does'nt exceed three. This number of frequencies observed is that predicted for an isolated cycle with local symmetry C₁.

Table 6

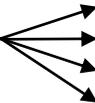
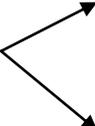
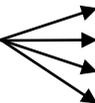
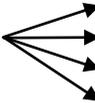
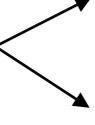
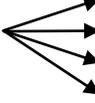
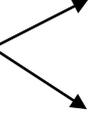
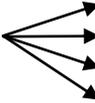
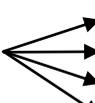
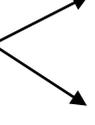
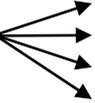
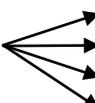
Isolated cycle P ₃ O ₉ with C _{3v} symmetry	local symmetry C ₁	Factor group C _i
v_{as} OPO ⁻ mode A ₁ IR, Raman →	v_{as} OPO ⁻ mode A IR, Raman 	v_{as} OPO ⁻ mode A _u IR, - v_{as} OPO ⁻ mode A _g -, Raman v_{as} OPO ⁻ mode A _u IR, - v_{as} OPO ⁻ mode A _g -, Raman
v_{as} OPO ⁻ mode E IR, Raman 	v_{as} OPO ⁻ mode A IR, Raman 	v_{as} OPO ⁻ mode A _u IR, - v_{as} OPO ⁻ mode A _g -, Raman v_{as} OPO ⁻ mode A _u IR, - v_{as} OPO ⁻ mode A _g -, Raman
v_s OPO ⁻ mode A ₁ IR, Raman →	v_s OPO ⁻ mode A IR, Raman 	v_s OPO ⁻ mode A _u IR, - v_s OPO ⁻ mode A _g -, Raman v_s OPO ⁻ mode A _u IR, - v_s OPO ⁻ mode A _g -, Raman
v_s OPO ⁻ mode E IR, Raman 	v_s OPO ⁻ mode A IR, Raman 	v_s OPO ⁻ mode A _u IR, - v_s OPO ⁻ mode A _g -, Raman v_s OPO ⁻ mode A _u IR, - v_s OPO ⁻ mode A _g -, Raman
v_{as} POP mode E IR, Raman 	v_{as} POP mode A IR, Raman 	v_{as} POP mode A _u IR, - v_{as} POP mode A _g -, Raman v_{as} POP mode A _u IR, - v_{as} POP mode A _g -, Raman
v_{as} POP mode A ₂ -, - →	v_{as} POP mode A IR, Raman 	v_{as} POP mode A _u IR, - v_{as} POP mode A _g -, Raman v_{as} POP mode A _u IR, - v_{as} POP mode A _g -, Raman
v_s POP mode E IR, Raman 	v_s POP mode A IR, Raman 	v_s POP mode A _u IR, - v_s POP mode A _g -, Raman v_s POP mode A _u IR, - v_s POP mode A _g -, Raman
v_s POP mode A ₁ IR, IR, Raman →	v_s POP mode A IR, Raman 	v_s POP mode A _u IR, - v_s POP mode A _g -, Raman v_s POP mode A _u IR, - v_s POP mode A _g -, Raman

Table 7: Separation of the internal modes of the $P_3O_9^{3-}$ cycles into stretching and bending modes

Four $P_3O_9^{3-}$ cycles of the unit-cell	IR	Raman
Active internal modes (total)	60 A_u	60 A_g
Stretching modes	24 A_u	24 A_g
Bending modes	36 A_u	36 A_g

Theoretical group analysis leads to the following correlation diagram :

isolated cycle $P_3O_9^{3-}$ with C_{3v} symmetry	site group C_1	factor group C_i
A_1	A	A_g
A_2		A_u
E		

3. Conclusion

Two new condensed phosphates have been prepared and characterized. $SrTi_4(P_3O_9)_2$ was prepared by the method of ion exchange resin and $NiRb_4(P_3O_9)_2$ was obtained by total thermal dehydration of $NiRb_4(P_3O_9)_2 \cdot 6H_2O$. The first new phosphate, the cyclotriphosphate $SrTi_4(P_3O_9)_2$, belonging to previously investigated structure types, has been characterized on the basis of its isotype $MgTi_4(P_3O_9)_2$. The second compound is the triphosphate $NiRb_4(P_3O_9)_2$ whose atomic arrangement is not yet known. The unit-cell dimensions of these two new condensed phosphates $SrTi_4(P_3O_9)_2$ and $NiRb_4(P_3O_9)_2$ have been calculated by means of the computer program TREOR.

We have examined and interpreted the IR spectrum of $SrTi_4(P_3O_9)_2$ in the light of the crystalline structure of its isotypic compound, of our results of calculations of the IR fundamental frequencies of the cycle $P_3O_9^{3-}$ with high symmetry D_{3h} and the successive isotopic substitutions of the equivalent atoms ^{31}P - ^{33}P , $^{16}O_i$ - $^{18}O_i$ and $^{16}O_e$ - $^{18}O_e$, of the three equivalent atoms (3P, 3O_i and 6O_e) belonging to the $P_3O_iO_e$ ring. The vibrational spectrum of $NiRb_4(P_3O_9)_2$ was examined and interpreted in the domain of the stretching vibrations of the P_3O_9 rings. The nature of the bending vibrations corresponding to the different observed bands was given. The interpretation of the infrared (IR) spectrum of $NiRb_4(P_3O_9)_2$

and vibrations analysis of the four cycles $P_3O_9^{3-}$ contained in the cyclotriphosphate, $NiRb_4(P_3O_9)_2$, was performed.

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