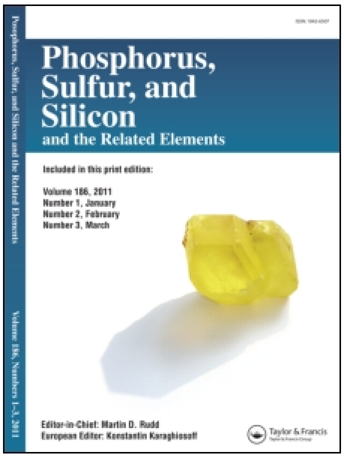

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Chemical Preparation, Crystallographic Data, Thermal Behavior, and IR Studies of $MnNa_4(P_3O_9)_2 \cdot 4H_2O$

K. Sbai[a]; S. BElaaouad[a]; K. BRouzi[a]
[a] Faculté des Sciences Ben M'sik Casablanca, Laboratoire de Recherches de Chimie-Physique Générale, Morocco

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CHEMICAL PREPARATION, CRYSTALLOGRAPHIC DATA, THERMAL BEHAVIOR, AND IR STUDIES OF $MnNa_4(P_3O_9)_2{\cdot}4H_2O$

K. Sbai, S. Belaaouad, and K. Brouzi
Laboratoire de Recherches de Chimie-Physique Générale,
Faculté des Sciences Ben M'sik Casablanca, Morocco

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Chemical preparation, crystallographic data, thermal behavior, and IR studies are given for two cyclotriphosphates $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ *and its anhydrous form* $MnNa_4(P_3O_9)_2$. $MnNa_4(P_3O_9)_2{\cdot}4H_2O$, *isotypic of* $CuK_4(P_3O_9)_2{\cdot}4H_2O$, *is monoclinic* $P2_1/a$ *with the following unit-cell dimensions:* $a = 8.536(2)$ Å, $b = 14.309(3)$ Å, $c = 8.508(2)$ Å, $\beta = 96.452(2)^\circ$ *and* $Z = 2$. $MnNa_4(P_3O_9)_2$, *isotypic of* $CaNa_4(P_3O_9)_2$, *is monoclinic* $C2/c$ *with the following unit-cell dimensions:* $a = 13.198(2)$ Å, $b = 8.241(1)$ Å, $c = 14.228(2)$ Å, $\beta = 95.045(1)^\circ$ *and* $Z = 4$. *The thermal behavior has been investigated and interpreted by comparison with IR absorption spectrometry and x-ray diffraction experiments.*

Keywords: Chemical preparation; crystallographic data; infrared spectrometry; thermal analyses (TGA-DTA); thermal behavior; x-ray diffraction

INTRODUCTION

During a systematic investigation of cyclotriphosphates of monovalent cations M^I ($M^I = Na^+$, K^+, Ag^+, and $NH_4{}^+$) and manganese, two forms of the sodium and manganese salts $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ and its anhydrous form $MnNa_4(P_3O_9)_2$ have been synthesized. Three cyclotriphosphates $MnK_4(P_3O_9)_2$,[1] $Mn(NH_4)_4(P_3O_9)_2{\cdot}6H_2O$,[1] and $MnAg_4(P_3O_9)_2{\cdot}6H_2O$[2] have already been prepared and characterized. The present work reports the chemical preparation, crystallographic data, thermal behavior and IR studies of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ and its anhydrous form $MnNa_4(P_3O_9)_2$.

The authors thank Professor A. Durif (CNRS, Grenoble, France) for the discussions and the bibliography.

Address correspondence to K. Sbai, Laboratoire de Reserche de Chemie Physique, Department de Chemie, Universite Hassan II Mohammedia, BP 77055, Casablanca, Morocco. E-mail: kacemsbai@mailcity.com

RESULTS AND DISCUSSION

Crystal Data

$MnNa_4(P_3O_9)_2{\cdot}4H_2O$ is isotypic of $CuK_4(P_3O_9)_2{\cdot}4H_2O$ whose atomic arrangement was determined by Durif and Averbuch-Pouchot.[3] $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ is monoclinic $P2_1/a$ with the following unit-cell dimensions: $a = 8.536(2)$ Å, $b = 14.309(3)$ Å, $c = 8.508(2)$ Å, $\beta = 96.452(2)^\circ$ and $Z = 2$.[4]

$MnNa_4(P_3O_9)_2$ is isotypic of $CaNa_4(P_3O_9)_2$ whose crystal data were reported by Grenier et al.[5] $MnNa_4(P_3O_9)_2$ is monoclinic $C2/c$ with the following unit-cell dimensions: $a = 13.198(2)$ Å, $b = 8.241(1)$ Å, $c = 14.228(2)$ Å, $\beta = 95.045(1)^\circ$ and $Z = 4$.[4] The x-ray diffractograms of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ and its anhydrous form $MnNa_4(P_3O_9)_2$ are reported in Figure 1.

Infrared Study

$MnNa_4(P_3O_9)_2{\cdot}4H_2O$ is isotypic of $CuK_4(P_3O_9)_2{\cdot}4H_2O$[3] and crystallizes in the monoclinic system, space group $P2_1/a$ (C^5_{2h}) with two formula units per unit-cell. The IR absorption spectra of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ and $MnNa_4(P_3O_9)_2$ are reported in Figure 2. The IR spectrum of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ (Figure 2a) reveals the presence of four bands due to water molecules in the domain 4000–1600 cm^{-1}: 3522, 3340, 3262 cm^{-1} are attributed to the stretching vibrations (ν O—H) of water molecules and the band at 1658 cm^{-1} represents the bending vibration (δ HOH) of water molecules. The band at 3262 cm^{-1} suggests the existence of hydrogen bond.[6] The valence vibration bands related to the $P_3O_9{}^{3-}$ rings are expected in the domain 1400–630 cm^{-1},[7–13] as well as possible bands due to interactions between $P_3O_9{}^{3-}$ rings and water molecules and also of water vibration modes. The IR spectrum of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ has been analysed on the basis of vibrational spectra of its crystalline structure and in the light of the calculation of the normal IR frequencies of the $P_3O_9{}^{3-}$ ring with D_{3h} symmetry. The local P_3O_9 symmetry is C_1, according to the $CuK_4(P_3O_9)_2{\cdot}4H_2O$ structure and yields to 30 normal modes active in IR and Raman and are distributed between valence and Raman, 30A. Such modes are distributed between valence and deformation modes as $\Gamma_{val.} = 12A$ (IR, Ra) and $\Gamma_{def.} = 18A$ (IR, Ra). For the valence vibrations, nine or ten vibrations are expected for a free cycle, as evidenced by the structural determination. Therefore one can neglect the perturbations related to the presence of four cycles and eight water molecules inside the unit-cell. The correspondence between free $P_3O_9{}^{3-}$, D_{3h}, valence vibrations and local symmetries is presented in Table I.

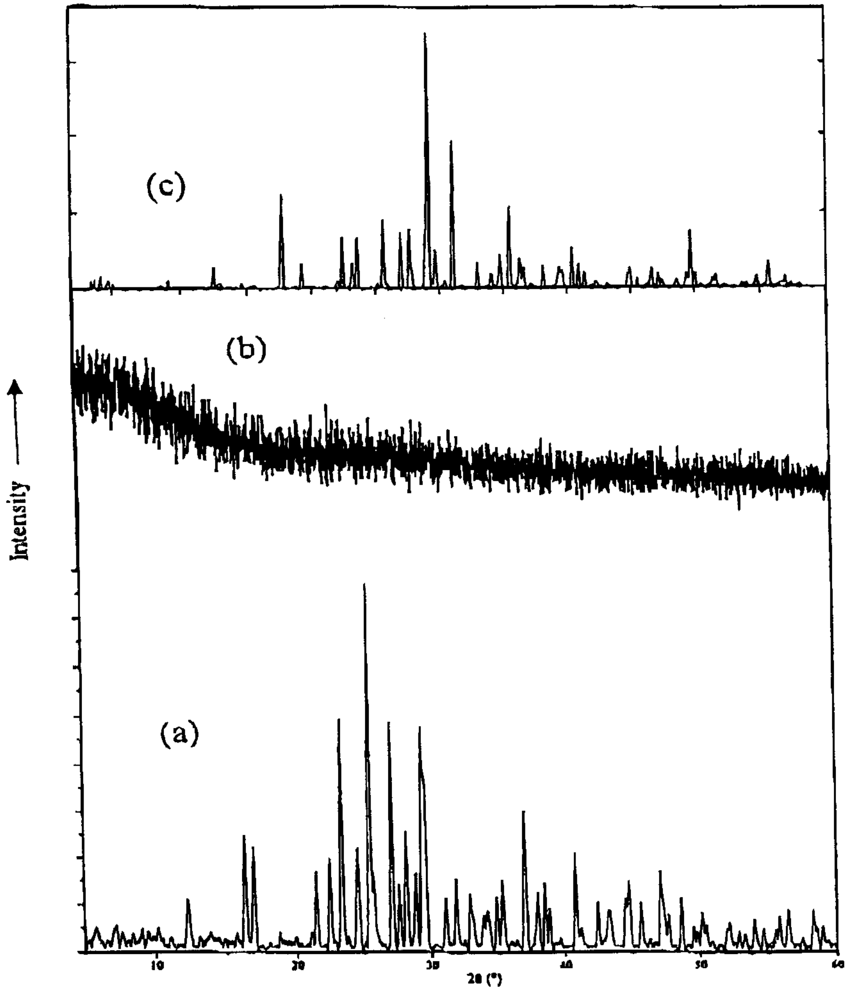

FIGURE 1 X-ray powder diffractograms of the phosphates: (a) $MnNa_4(P_3O_9)_2 \cdot 4H_2O$; (b) amorphous phase; and (c) $MnNa_4(P_3O_9)_2$.

Thermal Behavior

The two curves corresponding to the TGA and DTA analyses in air atmosphere and at a heating rate 6°C/min of $MnNa_4(P_3O_9)_2 \cdot 4H_2O$ are shown in Figure 3. The thermal analysis curve shows that the cyclotriphosphate $MnNa_4(P_3O_9)_2 \cdot 4H_2O$ undertakes at 184 and 233°C two endothermic dehydrations well confirmed by the weight loss observed on the TGA curve between 150°C and 390°C.

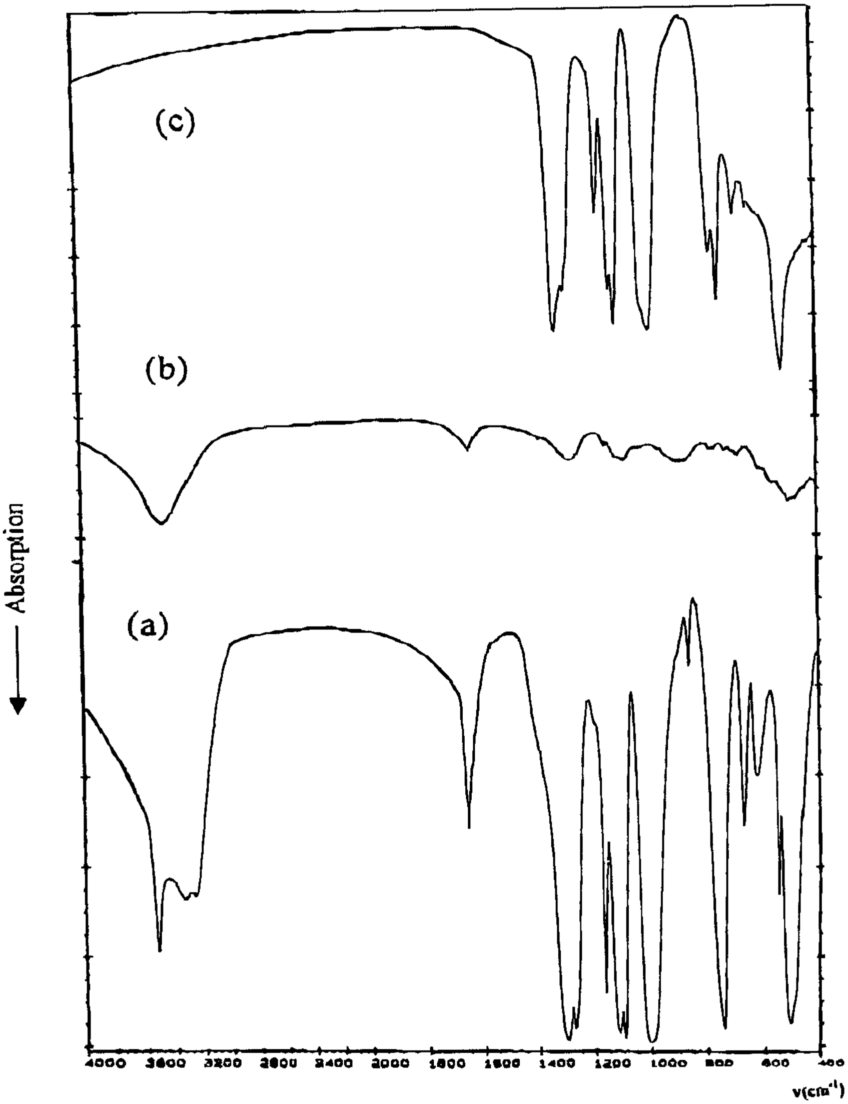

FIGURE 2 IR spectra of the phosphates: (a) $MnNa_4(P_3O_9)_2{\cdot}4H_2O$; (b) amorphous phase; and (c) $MnNa_4(P_3O_9)_2$.

The thermal behavior of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ was also studied in a step manner of temperature by x-ray diffraction and IR absorption between 20°C and 650°C. $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ is stable until 70°C. The removal of just two water molecules of hydration of

TABLE I Comparison of Free P_3O_9 Cycle Valence Frequencies Calculated for D_{3h} and C_1 Symmetries of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ (I) and $MnNa_4(P_3O_9)_2$ (II)

Molecular group D_{3h}				Site symmetry C_1		
ν_{cal} (cm^{-1})	I/I_{max}	Vibration	Mode activity	Mode activity	(I)	(II)
1288	55.30	$\nu_{as}PO_2$	A''_2 (IR, -) →	A (IR,Ra)	1307	1307
				A (IR,Ra)	1264	1279
1272	0	$\nu_{as}PO_2$	E″ (-, Ra)			
1272	0					
				A (IR,Ra)		
				A (IR,Ra)		
1225	100	$\nu_{as}POP$	E′ (IR,Ra)			
1225	100			A (IR,Ra)		
1169	0	ν_sPO_2	A'_1 (-, Ra) →	A (IR,Ra)	1166	1159
				A (IR,Ra)	1117	1117
					1089	1103
1108	5.86	ν_sPO_2	E′ (IR,Ra)			
1108	5.86			A (IR,Ra)		
1059	0	$\nu_{as}POP$	A'_2 (-, -) →	A (IR,Ra)	1011	977
				A (IR,Ra)	857	857
781	18.34	ν_sPOP	E′ (IR,Ra)			
						773
781	18.34			A (IR,Ra)	745	738
671	0	ν_sPOP	A'_1 (-, Ra) →	A (IR,Ra)	675	681

$MnNa_4(P_3O_9)_2{\cdot}4H_2O$, observed in the temperature range 80–150°C, destroyed the crystalline network yielding to an intermediate amorphous phase (Figure 1b) which does not exhibit the IR absorption bands characteristic of a cyclic phosphate (Figure 2b).[7–13] The amorphous product is probably, and according to Van Wazer and Holst,[14] the mixture of oxides MnO, Na_2O, and P_2O_5. From 250°C, the atomic rearrangement of MnO, Na_2O, and P_2O_5 occurs and provokes the start of crystallization of ring phosphate $MnNa_4(P_3O_9)_2$ (Figures 1c and 2c). The water characteristic vibrations have disappeared after the complete dehydration at 300°C (Figure 2c). The product of the total dehydration of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ between 300°C and 600°C is a new anhydrous cyclotriphosphate $MnNa_4(P_3O_9)_2$ characterized in the present sudy. With further increase in temperature, $MnNa_4(P_3O_9)_2$ remains stable and melts at 620°C. The third endothermic peak observed on the DTA curve (Figure 3) at 614°C corresponds to a melting point of $MnNa_4(P_3O_9)_2$.

By means of the DTA and the Kissinger method[15] used chiefly for studying the dehydration and the decomposition of hydrated and

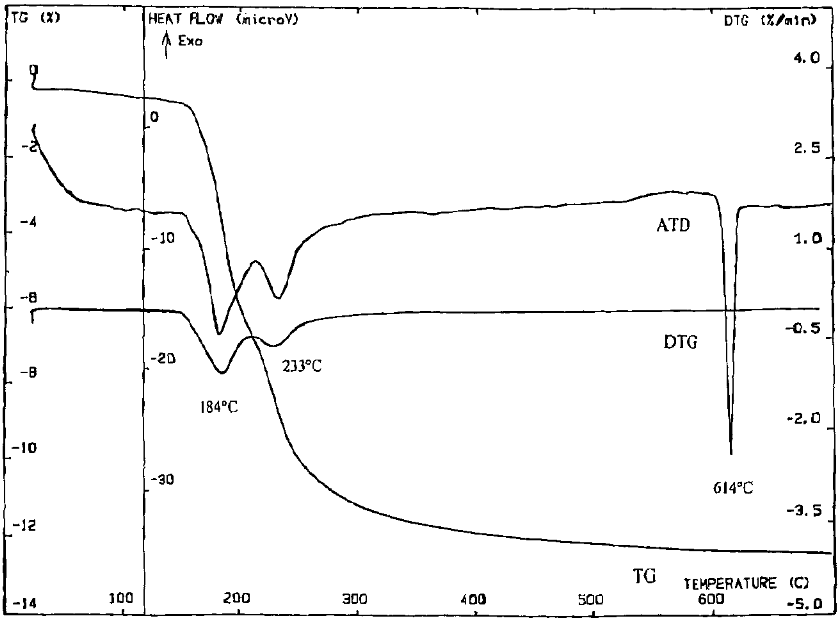

FIGURE 3 TGA and DTA curves of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ at rising temperature (6°C/min).

anhydrous solids, we calculated the activation energy of dehydration of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ which occurs in two stages: 51.79 kJ mol^{-1} for the loss of two water molecule and 47.44 kJ mol^{-1} for the loss of two water molecules (Figure 4).

CONCLUSION

From the global TGA weight loss curve, and the final phase $MnNa_4(P_3O_9)_2$ of the calcination of the title compound, we deduce the formula $MnNa_4(P_3O_9)_2{\cdot}4H_2O$, which the characterization by x-ray diffraction and infrared spectrometry confirm. So, the thermal behavior of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ can be summarized by the following schema:

$$MnNa_4(P_3O_9)_2{\cdot}4H_2O \xrightarrow{100\text{–}150^\circ C} MnO + 2Na_2O + 3P_2O_5 + 2H_2O$$

$$\xrightarrow{300\text{–}600^\circ C} MnNa_4(P_3O_9)_2 + 2H_2O$$

$$\xrightarrow{620^\circ C} \text{Melt of } MnNa_4(P_3O_9)_2$$

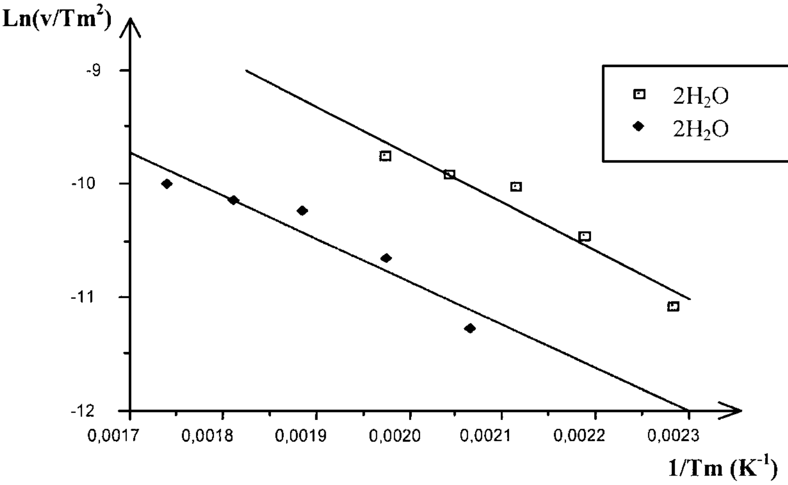

FIGURE 4 Ln $(v/Tm^2) = f(1/Tm)$ for $MnNa_4(P_3O_9)_2{\cdot}4H_2O$.

EXPERIMENTAL

Chemical Preparation

Crystals of the title compound were prepared by adding slowly dilute cyclotriphosphoric acid to an aqueous solution of manganese carbonate and sodium carbonate with a stoichiometric ratio Na/Mn = 4, according to the following chemical reaction:

$$2H_3P_3O_9 + MnCO_3 + 2Na_2CO_3 + 1H_2O$$
$$\rightarrow MnNa_4(P_3O_9)_2{\cdot}4H_2O + 3CO_2$$

The so-obtained solution was then slowly evaporated at room temperature until polycrystalline samples of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ were obtained. The cyclotriphosphoric acid used in this reaction was prepared from an aqueous solution of $Na_3P_3O_9$ passed through an ion-exchange resin "Amberlite IR 120."[16] $Na_3P_3O_9$ was obtained by thermal treatment of sodium dihydrogenomonophosphate, at 530°C for 5 h in air according to:

$$3NaH_2PO_4 \rightarrow Na_3P_3O_9 + 3H_2O$$

The weight loss performed by slowly heating up to a temperature of 300°C, confirms the compound as a tetrahydrate, $MnNa_4(P_3O_9)_2{\cdot}4H_2O$.

$MnNa_4(P_3O_9)_2$ was obtained as polycrystalline samples by total dehydration of $MnNa_4(P_3O_9)_2{\cdot}4H_2O$ under atmospheric pressure between 300 and 600°C.

Cyclotriphosphates, $MnNa_4(P_3O_9)_2{\cdot}4H_2O$, and its anhydrous form $MnNa_4(P_3O_9)_2$, described in the present work are stable for years in normal conditions of temperature and hygrometry.

$MnNa_4(P_3O_9)_2{\cdot}4H_2O$ and $MnNa_4(P_3O_9)_2$ have been studied through different techniques with experimental conditions described below.

INVESTIGATION

X-ray Diffraction

Powder diffraction patterns were registered with a SIEMENS diffractometer type D 5000 using CuKα1 radiation ($\lambda = 1.5406$ Å).

Infrared Spectrometry

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

Thermal Behavior

Thermal analyses TGA-DTA coupled were performed using the multimodule 92 Setaram Analyzer operating from room temperature up to 1400°C, in a platinum crucible, at various heating rates from 1 to 15°C/min.

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