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K. Brouzi^a; A. Ennaciri^b; F. Capitelli^c; V. Valentini^d; G. Mattei^d; M. Harcharras^b

^a Ecole Supérieure de Technologie Salé, University Mohammed V, Morocco ^b University Ibn Tofail, Kenitra, Morocco ^c CNR—Istituto di Cristallografia, Bari, Italy ^d CNR—Istituto di Metodologie Inorganiche e dei Plasmi, Roma, Italy

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Vibrational Study of Manganese Ammonium Dihydrogendiphosphate Hydrated $Mn_{0.5}NH_4H_2P_2O_7 \cdot H_2O$

K. Brouzi

University Mohammed V, Ecole Supérieure de Technologie Salé,
Morocco

A. Ennaciri

University Ibn Tofail, Kenitra, Morocco

F. Capitelli

CNR—Istituto di Cristallografia, Bari, Italy

V. Valentini

G. Mattei

CNR—Istituto di Metodologie Inorganiche e dei Plasmi, Roma, Italy

M. Harcharras

University Ibn Tofail, Kenitra, Morocco

Raman and infrared spectra of manganese ammonium dihydrogendiphosphate hydrated $Mn_{0.5}NH_4H_2P_2O_7 \cdot H_2O$ have been collected and interpreted using factor group analysis. Non-coincidence of the Raman and infrared spectra bands confirms a centrosymmetric structure for $Mn_{0.5}NH_4H_2P_2O_7 \cdot H_2O$, as previously investigated by X-ray structural study, as well as the joint appearance of ν_{as} POP and ν_s POP point to a bent POP configuration.

Keywords Bent POP configuration; dihydrogendiphosphates; factor group analysis; infrared spectra; Raman spectra

INTRODUCTION

Inorganic acidic diphosphates are compounds widely investigated because of their piezoelectrics, luminescent and ceramic properties.¹ Among the different classes of such phosphates we quote $AB(H_2P_2O_7) \cdot nH_2O$ where *A* and *B* are mono- and dicationic species. Detailed

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Address correspondence to K. Brouzi, Laboratoire d'Environnement, Ecole Supérieure de Technologie-Salé, B.P.: 227 Salé Médina, Morocco. E-mail: k.brouzi@caramail.com

structural studies are available in literature,² but vibrational spectroscopic investigations are lacking. In earlier works of ours, we have recently analyzed the $\text{NaMg}_{0.5}(\text{H}_2\text{P}_2\text{O}_7) \cdot 2\text{H}_2\text{O}$ ³ and $\text{KMg}_{0.5}(\text{H}_2\text{P}_2\text{O}_7) \cdot \text{H}_2\text{O}$ ⁴ species, measuring Raman and infrared vibrational spectra. In this article we report the vibrational study of the title compound to check its structural relationships and vibrational behavior.

RESULTS AND DISCUSSION

Factor Group Analysis

Crystal Structure

$\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ diphosphate crystallizes in the triclinic system, space group $P\bar{1}(C_i^1)$, with two molecules per cell with the following unit cell dimensions: (a) = 7.0029(2) Å, (b) = 7.4401(2) Å, (c) = 7.8771(2) Å, α = 80.444(1)°, β = 71.359(1)°, γ = 87.408(1)°, V = 383.48(2) Å³.⁵ All the atoms occupy general position, except Mn which is at special position (0, 1/2, 0) with site occupancy of 1/2 (Table I). The framework is made up of layers of MnO_6 octahedra, $\text{H}_2\text{P}_2\text{O}_7$ double tetrahedra groups and $(\text{NH}_4)^+$ ammonium cations, joint by strong hydrogen bonds. The $\text{H}_2\text{P}_2\text{O}_7$ double tetrahedron group possesses three types of P-O distances: P-O_{terminal}, which range from 1.490(1) up to 1.505 (1) Å; P-OH with values of 1.550(1) and 1.551(1) Å; and P-O_{bridge}, with values of 1.600(1) and 1.604(1) Å. The $\text{H}_2\text{P}_2\text{O}_7$ group displays bent eclipsed conformation, as depicted in Figure 1, while the bridge angle P1-04-P2 is 131.70(6)°.

Spectral Predictions

We can use the factor group analysis in order to predict the distribution of irreducible representations of external and internal vibrations modes for $\text{Mn}_{0.5}\text{NH}_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$. For the latter salt, the separation of the vibrations into internal and external modes in the factor group C_i of the $\text{H}_2\text{P}_2\text{O}_7$, H_2O , NH_4^+ and Mn^{2+} entities are given in Table II.

TABLE I Symmetry of the Sites Occupied in $\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$

Atoms	NH_4^+	Mn^{2+}	O(b)	H_2O
Sites	C_1	C_3	C_1	C_1

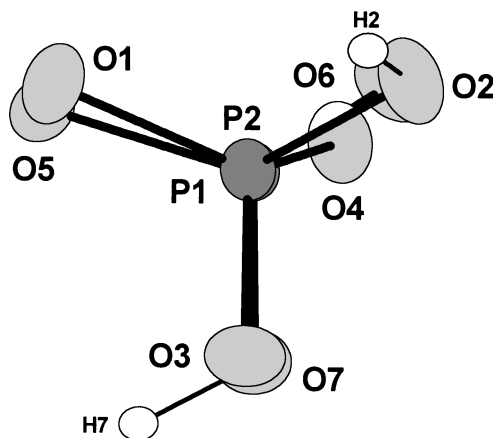


FIGURE 1 Bent eclipsed conformation of $\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$.⁵

The irreducible representation of the title compound in the C_i factor group (excluding acoustic modes) is:

$$\Gamma_{102} = 51 A_u + 51 A_g$$

The internal modes of $\text{H}_2\text{P}_2\text{O}_7^{2-}$, H_2O , and NH_4^+ in the $\text{Mn}_{0.5}\text{NH}_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ salt are given respectively by the correlation scheme (Tables III, IV and V).

The factor group analysis predicts the distribution of irreducible representation of the internal modes of $\text{H}_2\text{P}_2\text{O}_7^{2-}$ and NH_4^+ ions and H_2O molecules in $\text{Mn}_{0.5}\text{NH}_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ to be as follows:

$$\Gamma(\text{H}_2\text{P}_2\text{O}_7^{2-}) = 27 A_g (\text{Ra}) + 27 A_u (\text{IR})$$

$$\Gamma(\text{NH}_4^+) = 9 A_g (\text{Ra}) + 9 A_u (\text{IR})$$

$$\Gamma(\text{H}_2\text{O}) = 3 A_g (\text{Ra}) + 3 A_u (\text{IR})$$

TABLE II Summary of the Factor Group Analysis of $\text{Mn}_{0.5}\text{NH}_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$. Int.: Internal Modes, Ext.: External Modes, T: Translation Mode, L: Libration Mode

Factor group species C_i	$\text{H}_2\text{P}_2\text{O}_7$ C_1 -sites		H_2O C_1 -sites		NH_4^+ C_1 -sites		Mn^{2+} C_s -sites Ext.	Optical modes	Acoustic modes
	Int.	Ext.	Int.	Ext.	Int.	Ext.			
A_g	27	3L, 3T	3	3L, 3T	3	3L, 3T	0	51	0
A_u	27	3L, 3T	3	3L, 3T	3	3L, 3T	3T	54-3 = 51	3
Active modes	54	6L, 6T	6	6L, 6T	6	6L, 6T	3T	102	3

TABLE III Correlation Scheme for the Internal Modes of $\text{H}_2\text{P}_2\text{O}_7^{2-}$ in $\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$. IR: Infrared; Ra: Raman

Free ion group (C_{2v})	Site group (C_1)	Factor group (C_i)
9 A_1 (IR, Ra)	27A (IR, Ra)	27 A_g (Ra)
5 A_2 (Ra)	27A (IR, Ra)	
5 B_1 (IR, Ra)	27A (IR, Ra)	
8 B_2 (IR, Ra)	27A (IR, Ra)	27 A_u (IR)
Raman 27	27	27
Infrared 22	27	27
Coincidences 22	27	0

Interpretation of the Infrared and Raman Spectra of $\text{Mn}_{0.5}\text{NH}_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$

The Raman and infrared spectra of $\text{Mn}_{0.5}\text{NH}_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ are shown in Figures 2 and 3, respectively. Their bands assignments are given in Table VI. A comparison of the frequencies of the Raman and infrared bands shows that the majority of them are not coincident. This confirms that the diphosphate $\text{Mn}_{0.5}\text{NH}_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ possess a centrosymmetric structure, resulting in good agreement with our structural data.⁵ The interpretation of Raman and infrared spectra can be made on the basis of characteristic vibrations of PO_2 group, P—OH bond, POP bridge, NH_4 , and H_2O .^{3-4,6-8}

Vibrations of H_2O Molecules and NH_4^+ Ions

Broad bands in the region ($3600\text{--}3000\text{ cm}^{-1}$) correspond to the stretching vibration of both water molecules and NH_4^+ ions ($\nu\text{H}_2\text{O}$ and νNH_4^+).^{8,9} The splitting of the stretching and bending vibrations of water molecules in the range $3600\text{--}3000$ and $1730\text{--}1600\text{ cm}^{-1}$ in Raman and infrared spectra is probably due to the correlation field effect.¹⁰ The

TABLE IV Correlation Scheme for the Internal Modes of H_2O in $\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$

Molecular group (C_{2v})	Site group (C_1)	Factor group (C_i)
2 A_1 (Ra, IR)	3A(Ra, IR)	3 A_g (Ra)
1 B_2 (Ra, IR)	3A (Ra, IR)	3 A_u (IR)
Raman 3	3	3
Infrared 3	3	3
Coincidences 3	3	0

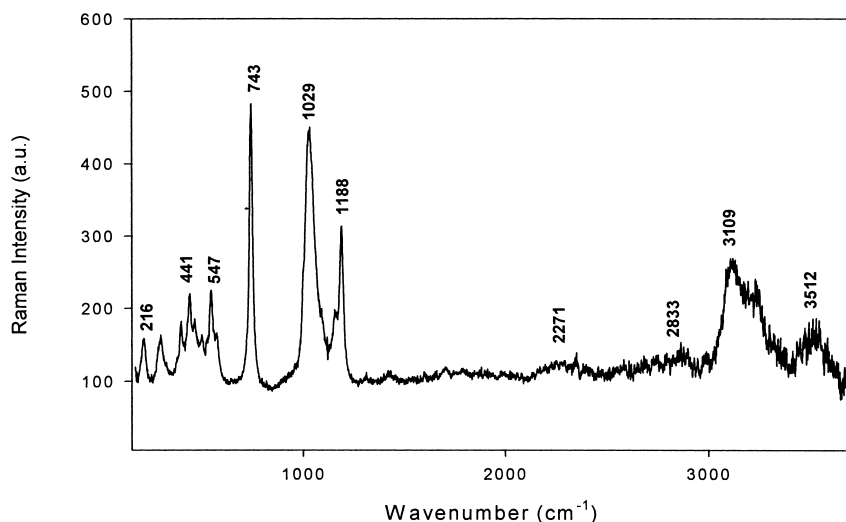
TABLE V Correlation Scheme for the Internal Modes of NH_4^+ in $\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$

Free ion group (Td)	Site group (C_1)	Factor group (C_i)
$1A_1$ (Ra)	$9A$ (IR, Ra)	$9 A_g$ (Ra)
$1 E$ (Ra)	$9A$ (IR, Ra)	
$2 T_2$ (IR, Ra)	$9A$ (IR, Ra)	$9 A_u$ (IR)
Infrared 2	9	9
Raman 4	9	9
Coincidences 2	9	0

bending vibrations of H_2O and NH_4^+ ions ($\delta \text{H}_2\text{O}$ and δNH_4^+) are seen in the range $1730\text{--}1600 \text{ cm}^{-1}$.^{8,9} δNH_4^+ is also observed in the range $1430\text{--}1380 \text{ cm}^{-1}$. The frequencies of νOH are localized in both Raman and infrared spectra in the range $3000\text{--}2270 \text{ cm}^{-1}$.^{3,4} The libration of water molecules $\rho \text{H}_2\text{O}$ is located at 665 and 647 cm^{-1} for infrared and Raman spectra respectively.^{3,4}

PO_2 Stretching Vibrations

The asymmetric and symmetric terminal-stretching vibrational-modes groups usually occur in the region $1200\text{--}985 \text{ cm}^{-1}$. The intense band

**FIGURE 2** Raman spectrum of $\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$.

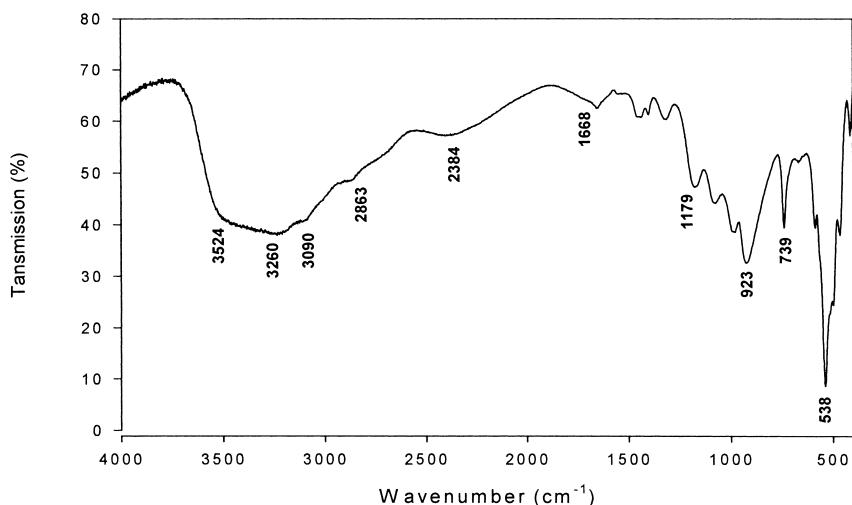


FIGURE 3 Infrared spectrum of $\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$.

observed in the Raman spectrum at 1029 cm^{-1} is attributed to the symmetric terminal P–O stretching vibration of the PO_2 group. In the infrared spectrum, the intense bands observed at 1179 cm^{-1} and 647 cm^{-1} is due to the asymmetric terminal stretching vibration of the PO_2 group.

The POP Bridge Stretching Vibrations

For the behavior of the POP bridge vibrations, two components are observed in Raman spectrum, $\nu_{\text{as}}\text{POP} = 942\text{ cm}^{-1}$ and $\nu_{\text{s}}\text{POP} = 743\text{ cm}^{-1}$, but three others in infrared spectrum at $\nu_{\text{as}}\text{POP} = 923\text{ cm}^{-1}$, $\nu_{\text{s}}\text{POP} = 739\text{ cm}^{-1}$, and 725 cm^{-1} which confirm the low symmetry of the cell.¹¹ This result confirms our structural data (the triclinic structure of $\text{Mn}_{0.5}\text{NH}_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$).⁵ The band located at 858 cm^{-1} in infrared spectrum and the one at 842 cm^{-1} in Raman spectrum are due to the ν P–OH mode.^{3,4}

The Deformation and Rocking of PO_2 , POP Deformation, Torsional Modes, and External Mode

The modes lying between $210\text{--}380\text{ cm}^{-1}$ in the Raman spectrum can be assigned to the external, torsional, and POP deformation modes; in the Raman spectrum, δPOP vibration is observed at 334 cm^{-1} ,¹² while the rocking and the PO_2 deformation modes are seen in the region $400\text{--}600\text{ cm}^{-1}$.¹¹

TABLE VI Vibrational Spectra Data (cm⁻¹) and Band Assignments of Mn_{0.5}NH₄H₂P₂O₇·H₂O

Raman frequency (cm ⁻¹)	IR frequency (cm ⁻¹)	Assignments
3512 ^{m,b}	3524 ^{s,b} 3397 ^{m,b}	ν H ₂ O + ν NH ₄
3215 ^{s,b}	3260 ^{s,b}	
3109 ^s	3090 ^{s,b}	
2833 ^{w,b}	2863 ^{m,b}	ν OH
2614 ^{v,w,b}		
2271 ^{w,b}	2384 ^{w,b}	
1794 ^{w,b}	1668 ^{w,b}	δ H ₂ O
1704 ^w		
1424 ^w	1446 ^w	δ NH ₄
1309 ^{vw}	1400 ^w 1319 ^w	
1188 ^s	1179 ^m	ν_{as} PO ₂
1156 ^m		+
1080 ^m	1079 ^m	ν_s PO ₂
1029 ^{v,s}	994 ^m	
942 ^{v,w,b}	923 ^s	ν_{as} POP
842 ^{v,w}	858 ^{m,b}	ν POH
743 ^{v,s}	739 ^m	ν_s POP
	725 ^w	
647 ^{v,w}	665 ^w	pH ₂ O
575 ^m	590 ^m	δ Po ₂
547 ^s	564 ^m	+
526 ^w	538 ^w	ρ PO ₂
501 ^m	514 ^w	
468 ^m	497 ^s	
441 ^s	462 ^s	
402 ^m	412 ^w	
334 ^w		δ POP
298 ^m		+
216 ^m		Torsional modes +
		External modes

^wWeak; ^mmedium; ^sstrong; ^vvery; ^bbroad.

One of the interesting aspects of this study is the possibility of obtaining direct information about the configuration of POP bridge from spectroscopic data. The ν^s POP vibrations are not observed in the infrared spectrum when the bridge is linear.¹¹ The appearance of ν_s POP at 725 and 739 cm⁻¹ in infrared spectrum indicates a bent configuration in Mn_{0.5}NH₄H₂P₂O₇·H₂O. This is in good agreement with our structural study (P1-O4-P2 = 131.70(6)°).⁵

CONCLUSION

In this paper, we have carried out a vibrational study of the triclinic diphosphate $\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$: we have established and interpreted infrared and Raman spectra of the compound using factor group analysis. The noncoincidence of the majority of the Raman and infrared spectra bands confirms a centrosymmetric structure of this salt. The appearance of both symmetric and asymmetric bridge stretching vibration in Raman and infrared spectra $\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ points to a bent POP bridge. This latter result is in good agreement with our X-ray study of $\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$.

EXPERIMENTAL

Synthesis

Solutions of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (0.1M), NH_4Cl (0.1 M), and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.1 M) were mixed with a few mL of concentrated HCl . The resulting solution was left at 30°C in bath of sand, and after 4 days pink crystals appeared. In the course of our study they were identified as $\text{Mn}_{0.5}\text{NH}_4\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$.⁵

Raman Spectroscopy

Micro-Raman measurements were performed in back-scattering geometry at room temperature by using a Dilor XY triple spectrometer with a liquid nitrogen cooled Charge Coupled Device (CCD) detector and an adapted Olympus microscope. The spectra were excited with an Ar^+ laser (514.5 nm, 3 mW) and focused onto a spot of $2\text{ }\mu\text{m}$ in diameter. The scattered light was not analyzed in polarization; spectral resolution was 0.5 cm^{-1} ; lines of a Ne lamp were used for frequency scale calibration.

FT-IR Spectroscopy

The infrared measurements were performed in transmission by a FT-IR Biorad spectrometer, FTS-40A with resolution of 2 cm^{-1} in the spectral range $400\text{--}4000\text{ cm}^{-1}$ using the KBr pellets technique (1 mg sample per 400 mg KBr).

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