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Vibrational analysis of $Ag_3(PO_2NH)_3$, $Na_3(PO_2NH)_3.H_2O$, $Na_3(PO_2NH)_3.4H_2O$, $[C(NH_2)_3]_3(PO_2NH)_3.H_2O$ and $(NH_4)_4(PO_2NH)_4.4H_2O$

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Abstract

FT IR and FT Raman spectra of $Ag_3(PO_2NH)$, (Compound **I**), $Na_3(PO_2NH)_3.H_2O$ (Compound **II**), $Na_3(PO_2NH)_3.4H_2O$ (Compound **III**), $[C(NH_2)_3]_3(PO_2NH)_3.H_2O$ (Compound **IV**) and $(NH_4)_4(PO_2NH)_4.4H_2O$ (Compound **V**) are recorded and analyzed on the basis of the anions, cations and water molecules present in each of them. The PO_2NH^- anion ring in compound **I** is distorted due to the influence of Ag^+ cation. Wide variation in the hydrogen bond lengths in compound **III** is indicated by the splitting of the v_2 and v_3 modes of vibration of water molecules. The NH_4 ion in compound **V** occupies lower site symmetry and exhibits hindered rotation in the lattice. The correlations between the symmetric and asymmetric stretching vibrations of P–N–P bridge and the P–N–P bond angle have also been discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Infrared spectrum; Raman spectrum; Trimetaphosphimate; Tetrametaphosphimate; Hydrogen bonding

1. Introduction

Many salts of trimetaphosphimic acid and tetrametaphosphimic acid were known more than 100 years ago [1,2]. These compounds have been mainly characterized by IR spectroscopy [3,4] and X-ray powder diffraction [5]. Extensive amount of work has been done on the study of the characteristic features of the coordination of metaphosphimate anions by vibrational spectroscopy, involving the calculation of wavenumbers and forms of the normal vibrations [6–16]. The trimetaphosphimate anion is a cyclic system formed by three regularly alternating slightly distorted PO_2NH tetrahedra. The confirmation of the ring in the chair form with symmetry close to

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C_{3v} has been established by X-ray structure analysis [17] and from the vibrational spectra of alkali metal trimetaphosphimates [9]. From a study of the vibrational spectra it is known that the tetrametaphosphimate anion in solution has S_4 symmetry and that in salts it has two kinds of structures, viz., C_{2h} symmetry and S_4 symmetry [14].

The present authors are interested in the study of the Raman and IR spectra of some newly synthesized phosphate compounds [18–20]. In this chapter a report of the analysis of both the IR and Raman spectra of $Ag_3(PO_2NH)_3$ (hereafter referred as compound **I**), Na_3 $(PO_2NH)3.H_2O$ (compound **II**), $Na_3(PO_2NH_3$ $.4H_2O$ (compound **III**), $[C(NH_2)_3]_3(PO_2NH)_3.H_2O$ (compound **IV**) and $(NH_4)_4(PO_2NH)_4.4H_2O$ (compound **V**) is made. The Raman spectra of these samples in aqueous solution are also recorded to clear the ambiguity regarding certain vibrations.

2. Experimental

The starting material $Na_2(PO_2NH)_3.4H_2O$ (compound **III**) was prepared by the method reported by Olthof et al. [17]. To an acidified solution of this compound, an aqueous solution of $AgNO_3$ is added to get $Ag_3(PO_2NH)_3$ (compound **I**) [21]. $Na_3(PO_2NH)_3.H_2O$ (compound **II**) was obtained by vapour diffusion of CH_3CH_2OH at 363 K into a 3×10^{-4} M aqueous solution of the starting material [22]. $[C(NH_2)_3]_3(PO_2NH)_3.H_2O$ (compound **IV**) was obtained by the addition of $[C(NH_2)_3]_2CO_3$ to a freshly prepared solution of $H_3(PO_2NH)_3$ [23]. For the preparation of $(NH_4)_4(PO_2NH)_4.4H_2O$ (compound **V**), the starting material $H_4(PO_2NH)_4.2H_2O$ was obtained according to the literature [6] by hydrolysis (333 K, 48 h) of $(PNCl_2)$, in dioxane. Then an aqueous solution of ammonia (10%) is added to a stoichiometric amount of the acid followed by precipitation with acetone [24].

Table 1
Crystallographic datas of the five compounds

Compounds	Crystallography	Space group	Z^B	Refs.
I	Monoclinic	$P2_1/c(C_{2h}^5)$	4	[21]
II	Monoclinic	$C2(C_2^3)$	2	[22]
III	Monoclinic	$P2_1/n(C_{2h}^5)$	4	[17]
IV	Orthorhombic	$Pbca(D_{2h}^{15})$	8	[23]
V	Monoclinic	$P2_1/n(C_{2h}^5)$	2	[24]

The IR and Raman spectra were recorded using a Bruker IFS 66V FT-IR/FT-Raman Spectrometer. The Raman spectra were recorded with a resolution of 4 cm^{-1}, using an Nd:YAG laser at wavelength 1.064 μm and power 200 mW, over the range 50–3500 cm^{-1}. The IR spectra are obtained in the range 400–4000 cm^{-1} with the samples as KBr pellets using a globar source.

3. Factor group analysis

The compounds **I**, **II**, **III** and **V** crystallizes in the monoclinic system and compound **IV** is orthorhombic. The crystal symmetry data of all the five compounds used in the present work are tabulated in Table 1.

The cations, anions and water molecules in all the compounds occupy general position. The trimetaphosphimate anion $(PO_2NH)_3^{3-}$ and tetrametaphosphimate anion $(PO_2NH)_4^{4-}$ exhibit chair conformation, but in compound **I** the anion is markedly distorted because of the interaction between Ag^+ and one nitrogen atom of the anion [21]. The $(PO_2NH)_3^{3-}$ ring has C_{3v} symmetry [13] and the $(PO_2NH)_4^{4-}$ ring has C_{2h} symmetry [15]. The cyclic anion rings in trimetaphosphimates are linked to one another by N–H---O hydrogen bonds to form pairs. These units are interconnected by O–H---O hydrogen bonds through water molecules forming columns. In compound **V** the tetrametaphosphimate rings are finked by N–H---O bonds forming column, along [100]. These columns are interconnected by O–H---O and N–H---O hydrogen bonds through water molecules and ammonium ions [21–24]. All H atoms are involved in hydrogen bonding. In **II** and **III** the sodium ions are approximately octahedrally coordinated by six oxygen atoms, either from the phosphonate groups or from the water molecules. The factor group analysis using the standard correlation method [25], for each compound gives the irreducible representation at $k = 0$ as

Compound **I**	$54A_g(R)+54B_g(R)+53A_u(IR)+52B_u(IR)$
Compound **II**	$62A(R,IR)+61B(R, IR)$
Compound **III**	$90A_g(R)+90B_g(R)+89A_u(IR)+88B_u(IR)$
Compound **IV**	$144A_g(R)+144B_{1g}(R)+144B_{2g}(R)$ $+144B_{3g}(R)+144A_u(O)+143B_{1u}(IR)$ $+143B_{2u}(IR)+143B_{3u}(IR)$
Compound **V**	$78A_g(R)+78B_g(R)+77A_u(IR)+76B_u(IR)$

4. Results and discussions

The IR and Raman spectra recorded for all the five compounds under investigation are shown in Figs. 1–3. The observed spectral lines and their assignments are given in Table 2.

4.1. Vibrations of PO_2NH^- anion

Analysis of the spectra obtained shows that vNH modes are highly characteristic. These are obtained as weak bands in Raman and medium to strong in IR around 3170 cm^{-1} in all the five compounds. The multiplicity of bands observed in compound **I** may be due to the participation of the NH groups in intramolecular and intermolecular hydrogen bonding [13]. The frequency shift observed in compound **IV** may be attributed to the overlapping of the vNH vibrations with that of vNH$_2$ vibrations. The NH deformations are observed in the region 1390–1322 and 781–723 cm^{-1}.

As expected the asymmetric and symmetric stretching vibrations of PO_2 group are observed in the region 1241–1141 and 1118–1039 cm^{-1} respectively [26]. The asymmetric modes are very strong in the IR spectrum and the symmetric modes are very strong in the Raman spectrum. Both the asymmetric and symmetric stretching modes of PO_2 in compound **V** appear a little lower in frequency when compared to all the other four compounds. This is due to the greater value of the average P–O bond length in compound **V** than that in all the other compounds [24]. The bending modes of PO_2 group are observed around 600 cm^{-1}. The wagging, rocking and twisting modes of PO_2 group are also assigned (Table 2).

The ring vibrations of the anion — the antisymmetric and symmetric stretches of P–NH–P bridges are expected in the region 1000–800 cm^{-1} and the ring breathing vibration around 400 cm^{-1} [12,15]. In compound **I** the asymmetric stretching gives very weak Raman bands at 971 and 937 cm^{-1} and the symmetric stretching bands are observed at 831 and 793 cm^{-1}. The corresponding IR bands are singlets observed at 933 and 813 cm^{-1} respectively. The large splitting (≈ 138 cm^{-1}) of the symmetric mode observed in the Raman spectrum confirms the distortion of the PO_2NH^- anion ring due to the influence of the stronger Ag^+ cation on the anion structure [21]. In the Raman spectrum of compound **V**, a weak band is observed at 1008 cm^{-1}. Sukova et al. [15], in their studies on lanthanum and lanthanide tetrametaphosphimate had assigned the strong IR band around ≈ 1005 cm^{-1} to v_{as}P–NH–P along with its components in the region 980–900 cm^{-1}. Accordingly the Raman band at 1008 cm^{-1}, in the present study, is assigned to v_{as}P–NH–P. Its components are the very weak bands at 980–910 cm^{-1}.

The corresponding IR. bands are very strong at 992 and 955 cm^{-1}. The weak to medium intensity Raman bands around 493 cm^{-1} are due to the ring breathing vibrations. The IR spectra show medium to strong intensity bands in this region. The external deformation mode is assigned to the weak bands around 225 cm^{-1} [9,12].

4.2. Vibrations of NH_4^+ cation

The normal modes of vibration of free NH_4^+ ion under perfect T_d symmetry have frequencies of 3033, 1685, 3134 and 1397 cm^{-1} for $v_1(A_1)$, $v_2(E)$, $v_3(F_2)$ and $v_4(F_2)$ modes, respectively [26].

Table 2
Spectral data (cm^{-1}) and band assignments of $\mathrm{Ag_3(PO_2NH)_3}$, $\mathrm{Na_3(PO_2NH)_3.H_2O}$, $\mathrm{Na_3(PO_2NH)_3.4H_2O}$, $\mathrm{[C(NH_2)_3]_3(PO_2NH)_3.H_2O}$ and $\mathrm{(NH_4)_4(PO_2NH)_4.4H_2O}$[a]

$\mathrm{Ag_3(PO_2NH)_3}$		$\mathrm{Na_3(PO_2NH)_3.H_2O}$		$\mathrm{Na_3(PO_2NH)_3.4H_2O}$		$\mathrm{[C(NH_2)_3]_3(PO_2NH)_3.H_2O}$		$\mathrm{(NH_4)_4(PONH)_4.4H_2O}$		Assignments
Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	
							3586m		3571m	Combination
	3472wbr				3455m		3418s	3377vw	3353sh	
					3372m					$v_3\mathrm{H_2O}$
		3214w	3234s	3300wbr	3310m	3352w	3350sh	3301wbr		$v_1\mathrm{H_2O}$
									3265sh	$v_3\mathrm{NH_4}$
									3213sh	
3273w										
3233w	3223w									
	3151m	3173w	3168s	3173wbr	3173m	3198wbr	3126s		3162vs	$v\mathrm{NH}/v\mathrm{NH_2}$
3086vw	3049sh									
								3058vwbr	3018sh	$v_1\mathrm{NH_4}$
									2853m	Combination
	2684w		2678w		2704vvw				2716sh	
	2596vw		2659w		2644vvw					$v\mathrm{NH{-}{-}{-}N(O^-)}$
			2575w							
			2321vw						2359vw	Combinations and overtones
2208vw			2219w							
2119vw		2124vw	2185w						2145m	
				2085vwbr						
			1720w							
								1688vw	1699w	$v_2\mathrm{NH_4}$
	1643w		1686sh	1670vwbr	1694w	1649vw	1649sh		1653m	$v_2\mathrm{H_2O}$
					1661w					
					1693w					
							1663vs			$v_{as}\mathrm{CN}$
						1588vw	1442sh			$\delta\mathrm{NH_2}$
1471w			1545w							Combinations
									1461s	
								1420vwbr	1419sh	$v_4\mathrm{NH_4}$
									1402s	
1390vvw									1385sh	
1369vvw	1345s		1355sh		1355m				1362sh	$\delta\mathrm{NH}$
			1335vs		1326m		1322m		1343s	
					1281m		1296sh			$\delta\mathrm{O{-}H{-}{-}{-}O}$
					1241s					
	1226vs	1222w		1238m	1225s	1234vw				
			1211vs	1198m	1192m		1210s	1192sh	1201vs	$v_{as}\mathrm{PO_2}$

Table 2 (*Continued*)

$Ag_3(PO_2NH)_3$		$Na_3(PO_2NH)_3.H_2O$		$Na_3(PO_2NH)_3.4H_2O$		$[C(NH_2)_3]_3(PO_2NH)_3.H_2O$		$(NH_4)_4(PONH)_4.4H_2O$		Assignments
Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	
1167w		1185w	1187s	1182m		1174vw		1180w		
								1148w	1141s	
	1111m	1107vs	1101s	1107vs	1118w	1106m	1102m			
1094vs								1080vs		v_sPO_2
	1054vs	1059w	1060vs	1054m	1066vs				1063s	
1040w		1039w	1043vs	1047m	1054s	1049vw	1046vs			
						1007vs	1006w			
971vw								1008w	992s	
								980vw		v_{sa}P–NH–P
		955w	952vs	955vw	960s		946sh		955vs	
937vw	933vs			933vw	931s	921vvw	929s	910vw		
				845w	860vw	853vw		859vvw		
831vw	813m		826s		821m				818m	v_sP–NH–P
793m										
		803m		806w	802m					H_2O liberation
755s	774sh		781m				779sh			δNH
	731m			726m	740m	723wbr		745s		
		658vw	662m		650sh					
610s	602m	607m	599m	601m	608m	607vw	608m	596vvw	589m	δPO_2
	540s		542s					560w	556m	
							515w			δCN_3
		524m			536m	531m				
512w	504s		513s	517m	504m		493w		506s	Ring breathing
470w			480m	478m			492m	474w		
402							424sh	423w	421vw	
		374m		377sh		385sh				ωPO_2
				360s		351w		368s		
345w										
334w		318sh						332m		
297m		295m		297s		292w		288m		ρPO_2
						277w				
258vw		231vw		247w				228m		Ring deformation
								209m		
167sh				157vw				166m		ιPO_2
124m		131w		129vw		134s		137m		υN–H---O
		114sh				109sh		105m		vO–H---O
84s		84m		84m		83m		84m		External mode

[a] Relative intensities: v, very; w, weak; m, medium; s, strong; sh, shoulder; br, broad.

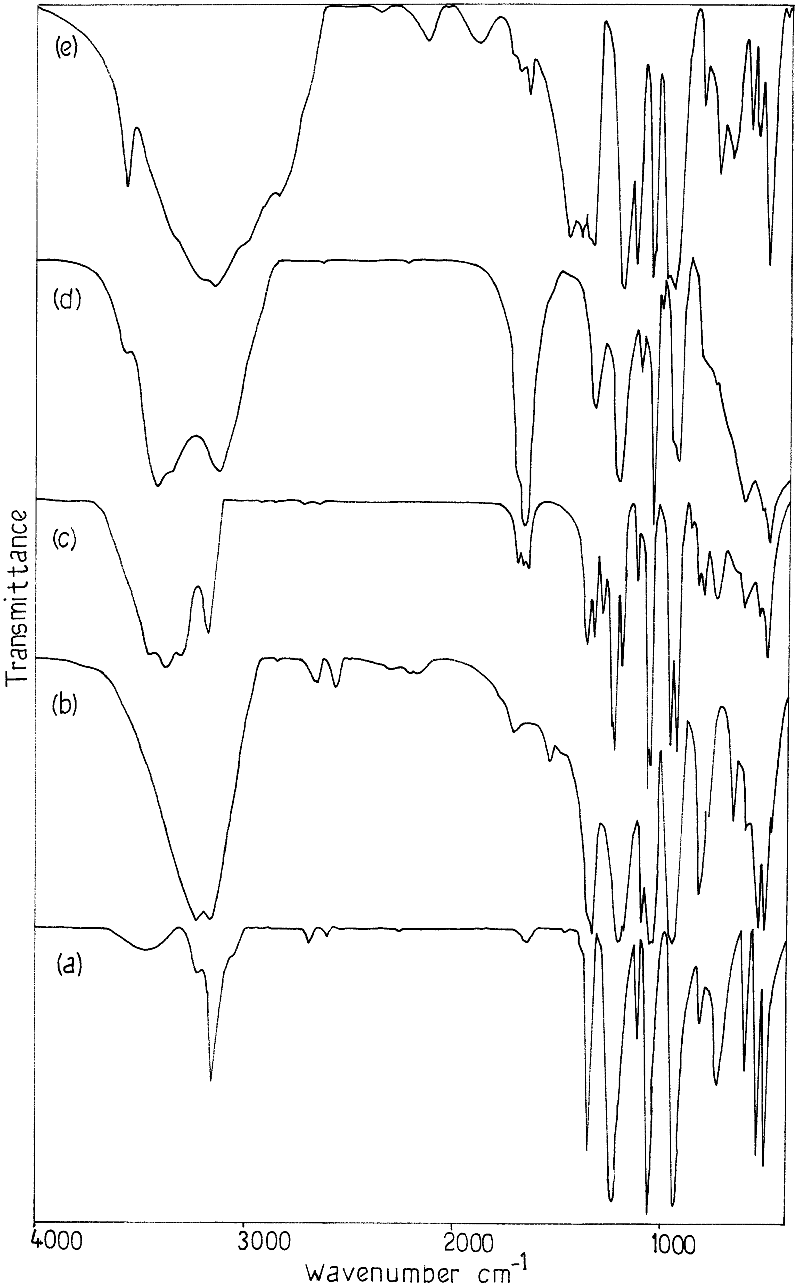

Fig. 1. FT IR spectra of (a) $Ag_3(PO_2NH)_3$, (b) $Na_3(PO_2NH)_3.H_2O$ (c) $Na_3(PO_2NH)_3.4H_2O$, (d) $[C(NH)_3]_3(PO_2NH)_3.H_2O$ and (e) $(NH_4)_4(PO_2NH)_4.4H_2O$ in the region 400–4000 cm^{-1}.

All the four modes are Raman active whereas v_1 and v_2 are IR inactive. In the crystal, the ion occupies a lower site symmetry, which may lead to the activation of inactive modes, splitting of degenerate modes and shifting of fundamental modes.

In the Raman spectrum of compound **V**, the weak broad band at 3058 cm^{-1} is assigned to the symmetric stretching mode υ_1. The corresponding IR band appears as a shoulder at 3018 cm^{-1}. The broadening (≈ 250 cm^{-1}) of the υ_1 mode indicate the participation of the NH_4 ions in the formation of different types of hydrogen bonds N–H---N and N–H---O of varying strength [27]. The struc-tural investigation of compound **V** [24] reports that the NH_4 ions take part in extended hydrogen bonding by bridging, via, the lone pairs of OW2, N4–H42---OW2---H31–N3 (N---O---N 2.801, 2.858 Å). The observation of strong IR band extending from about 3700 to 2700 cm^{-1} (FWHM ≈ 720 cm^{-1}) also supports this. The absorption shoulders at 3265 and 3213 cm^{-1} are due to the triply degenerate asymmetric stretching mode υ_3. The υ_2 mode is observed as weak absorption band at 1699 cm^{-1}. The very weak Raman band at 1688 cm^{-1} is the counterpart of this mode. The absorption triplet at 1461, 1419 and 1402 cm^{-1} are due to the triply degenerate υ_4 mode of the ammonium ion.

The splitting of the υ_3 and υ_4 mode and the activation of the IR inactive modes υ_1 and υ_2 supports the lowering of site symmetry (C_1) of the ion. All the four modes of the NH_4 ion are found to be shifted from the free state values. This observation, in agreement with the structural reports, shows that the ion is distorted from the ideal tetrahedral geometry [24].

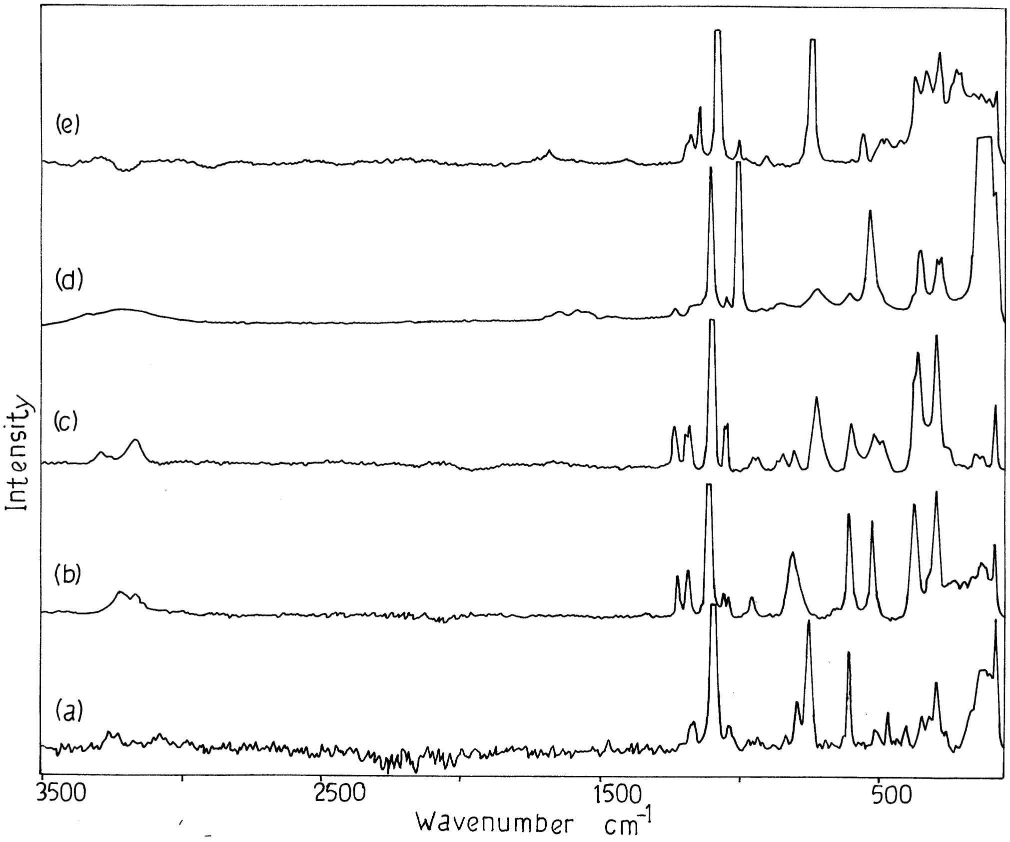

Fig. 2. FT Raman spectra of (a) $Ag_3(PO_2NH)_3$, (b) $Na_3(PO_2NH)_3.H_2O$ (c) $Na_3(PO_2NH)_3.4H_2O$, (d) $[C(NH_2)_3]_3(PO_2NH)_3.H_2O$ and (e) $(NH_4)_4(PO_2NH).4H_2O$ in the region 50–3500 cm^{-1}.

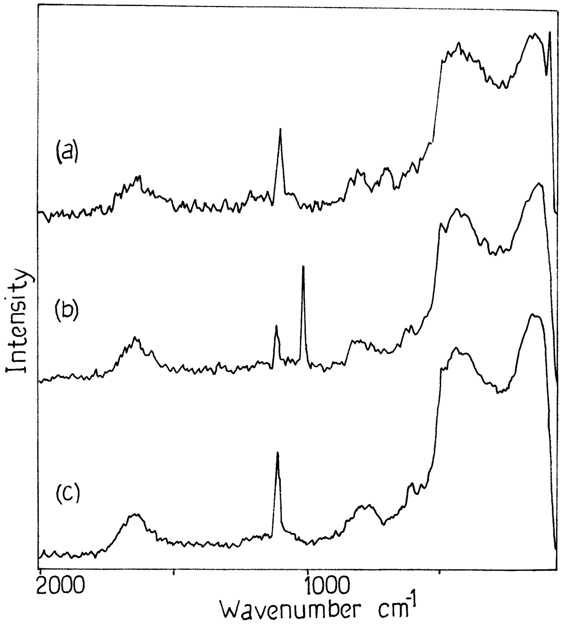

Fig. 3. FT Raman spectra of the aqueous solution of (a) $Na_3(PO_3NH)_3.H_2O$ (b) $[C(NH_2)_3]_3(PO_2NH)_3.H_2O$ and (c) $(NH_4)_4(PO_2NH)_4.4H_2O$ in the region 50–2000 cm^{-1}.

In a freely rotating NH_4 ion, the v_3 and v_4 modes are triply degenerate. However if it is in the locked-in position in the crystal lattice, the degeneracy is expected to be lifted [28]. In the present study, the removal of degeneracy of the v_3 and v_4 modes suggests that the ion is probably in a locked in position in the crystal lattice. The fundamental v_6 could not be identified independently as it merges in the region of the bending mode of PO_2. However, its combinations $v_2 + v_6$ and $v_4 + v_6$ are not observed. Hence it may be inferred that the NH_4 ion is executing hindered rotation in the lattice [29–32].

4.3. Vibrations of $[C(NH_2)_3]^+$ cation

In the structural studies of triguanidinium tri-μ-imido-cyclotriphosphate monohydrate (compound **IV**) Stock et al. have assigned highly intense IR band at 1662 cm^{-1} to the asymmetric CN stretching vibrations. The IR spectrum of tetraguanidinium tetra-μ-imido-cyclotetraphosphate tetrahydrate $[C(NH_2)_3]_4(PO_2NH)_4.4H_2O$ also shows a highly intense IR band at 1659 cm^{-1} due to v_{as}CN [28]. In the present investigation, the very strong absorption band at 1663 cm^{-1} is assigned to the asymmetric CN stretching vibrations. The very high intensity of this band differentiate it from the v_2 mode of water molecules, which are usually weak to moderate in IR. The symmetric CN stretching is very strong in Raman at 1007 cm^{-1}. Its corresponding IR band is weak at 1006 cm^{-1}. The high intensity of this band in the Raman spectra and the low intensity in the IR spectra, differentiate it from the v_{as}P–NH–P mode, which is usually weak in Raman and intense in IR. The Raman spectrum of the aqueous solution also shows, this intense band without much shift (1010 cm^{-1}), which support our assignment of v_sCN. The deformation of CN_3 gives a weak band at 515 cm^{-1}. The vNH$_2$ mode is masked in the broad bands of vNH. However, the bands of NH_2 deformation are clearly identifiable. The weak Raman band at 1588 cm^{-1} and the shoulder at 1542 cm^{-1} in the IR spectrum are due to the δNH$_2$ vibration.

4.4. Vibrations of water molecules

The v_1 and v_3 modes of water molecules are observed in the region 3472–3214 cm^{-1} and the bending mode v_2 around 1661 cm^{-1}. The existence of broad overlapping bands in the stretching region shows the presence of both weakly and strongly bonded molecules of water of crystallization and of hydrogen bridges with different bond energies. The absorption band at 3472 and 1643 cm^{-1} in the unhydrated compound **I** are due to the water molecules adsorbed during pelletization. In the IR spectrum of compound **III** the v_3 mode of H_2O appear as a doublet at 3455 and 3372 cm^{-1} and the v_2 mode as triplet at 1694, 1661 and 1639 cm^{-1}. This splitting of the fundamental vibrations are due to the wide variation in the hydrogen bond lengths, where the O---O ranges from 2.821 to 4.144 Å [17]. The librational modes of H_2O are observed as weak to medium intense bands in the region 806–802 cm^{-1}. This assignment is confirmed by the broad bands observed about this region in their solution spectra.

4.5. Hydrogen bonding

Structural investigations report that, in all the five compounds investigated, two anion rings are linked to each other by N–H---O hydrogen bonds forming pairs [17,21–24]. These units are interconnected by O–H---O hydrogen bonds through water molecules.

As a result of the comparison of the spectra of tetrametaphosphimates with NH group in the ring, with the spectrum of octa silver salt Ag_g $(PO_2N)_4$, Lunkwitz and Steger [7] were able to distinguish two bands at 3075 and 2675 cm^{-1} corresponding only to NH groups and bridging hydrogen bonds NH---N(O^-), respectively. The weak absorption bands in the region 2716–2575 cm^{-1} are accordingly assigned to NH...N(O^-) vibrations.

4.6. Correlation between the P–N–P stretching vibrations and the P–N–P angle

The correlation between the P–O–P angle and the asymmetric and symmetric stretching frequencies of the P–O–P bridge are well known [33–37]. The correlation exhibits a definite pattern of relationship. Several authors have used these correlations to calculate the unknown P–O–P angles in pyrophosphates [36,37] and cyclohexaphosphates [19]. Lazarev, [37] has used similar type of correlations in pyrosilicates and determined the Si–O–Si angles.

In the present investigation, a similar type of correlation is attempted for the P–N–P group. The structural and spectral data used are listed in Table 3. The curves (Fig. 4) are plotted for the two relationships

1. $v_{as}\text{PNP} - v_{as}\text{PNP} = f_1(\angle \text{PNP})$
2. $(v_{as}\text{PNP} - v_{s}\text{PNP})/(v_{as}\text{PNP} + v_{s}\text{PNP}) = f_2(\angle \text{PNP})$

The curves show a definite pattern as in the case of POP bridge.

Table 3
Correlation between the PNP bridge angle and its stretching vibrations

Compound	v_{as}PNP (cm^{-1})	v_sPNP (cm^{-1})	$v_{as}-v_s$ (cm^{-1})	$(v_{as}-v_s)/(v_{as}+v_s)$	∠PNP (°)	Refs.
$Ag_3(PO_2NH)_3$	933	813	120	0.0687	125.5	[21]; present work
$Na_3(PO_2NH)_3.H_2O$	952	826	126	0.0709	124.3	[22]; present work
$Na_3(PO_2NH)_3.4H_2O$	960	860	100	0.0549	121.0	[17]; present work
	931	821	110	0.0628	122.6	
		802	129	0.0744	124.4	
$[C(NH_2)_3]_3(PO_2NH)_3.H_2O$	921	853	68	0.0373	122.1	[23]; present work
$(NH_4)_4(PO_2NH)_4.4H_2O$	992	818	137	0.0773	128.61	[24]; present work
	955		174	0.0961	130.1	
$Rh(PO_2NH)_3(NH_3)_3.H_2O$	935	870	65	0.03601	121	[16]
$Na_4\{Cu[(PO_2NH)_3]_2\}.10H_2O$	960	820	110	0.0628	122	[15]
	930	800	160	0.0909	133	
$[C(NH_2)_3]_4(PO_2NH)_4.4H_2O$	976	820	121	0.0687	123	[23]
	941	773	156	0.0869	130	

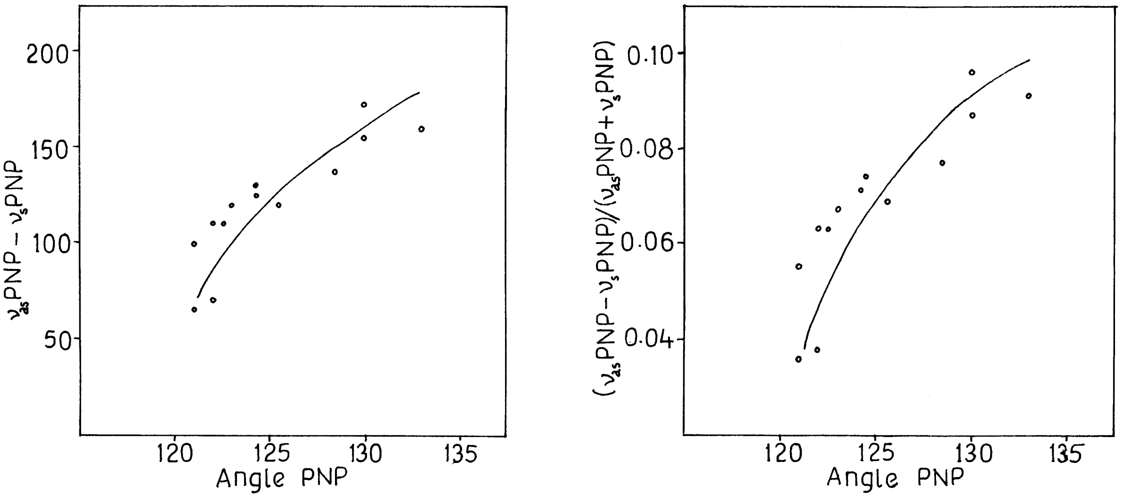

Fig. 4. Relationship between (a) the angle PNP and υ_{as}PNP – υ_sPNP and (b) the angle PNP and (υ_{as}PNP – υ_sPNP)/(υ_{as}PNP + υ_sPNP).

5. Conclusions

The large splitting of vs. P–NH–P modes in compound **I** indicates distortion of the PO_2NH^- anion ring due to the influence of Ag^+ cation. NH_4^+ ion exhibits hindered rotation in the lattice. The lifting up of the degeneracy of υ_3 and υ_4 mode and the activation of the IR inactive modes indicates lower site symmetry of the NH, ion. Splitting of the υ_2 and υ_3 modes of vibration of water molecules in compound **III** indicates the wide variation in the hydrogen bond lengths. The correlation between angle P–N–P and the stretching vibrations of the P–N–P bridge exhibit a definite pattern.

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