

THE INFRARED SPECTRA  
OF SOME METAL (II) AMMONIUM  
PHOSPHATES

**Introduction**

The infrared spectra of metal (II) ammonium phosphates have not received, enough, attention. The only infrared data concerning this interesting group of compounds are those of Corbridge and Lowe (1). In their article on the infrared spectra of some inorganic phosphorus compounds the authors report the frequencies of the absorption bands of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  and of  $\text{FeNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ . Whereas the frequencies reported for the latter compound are reasonably close to those we report here for the monohydrates of some other metal (II) ammonium phosphates, the frequencies for  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  do not agree with our values.

**Experimental**

The compounds studied were prepared by double decomposition of metal (II) salts (chlorides or sulfates) and  $(\text{NH}_4)_2\text{HPO}_4$ , the experimental conditions being similar to those described by Étienne and Boullé (2). The spectra of the sample in form of KBr pressed discs were recorded, using a Perkin-Elmer 221 infrared spectrophotometer.

**Results**

Table I summarizes the absorption frequencies (in  $\text{cm}^{-1}$ ) of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  (I),  $\text{NiNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  (II),  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  (III),  $\text{NiNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  (IV),  $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  (V),  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  (VI) and  $\text{ZnNH}_4\text{PO}_4$  (VII), as well as tentative assignments for the main absorption bands.

TABLE I  
Infrared spectra of some metal (II) ammonium phosphates\*

I	II	III	IV	V	VI	VII	Assignment
3590 sh 3500 sh 3250 s 3100 s	3450 sh	3430 s	3395 s	3400 s	3415 s		OH stretching
	3200 s	3220 s	3205 s	3220 s	3230 s	3250 sh	OH stretching
	3110 s	3040 s	3030 s	3020 s	3020 s	3175 s	and/or $\nu_1$ and
						3150 m	$\nu_3$ of $\text{NH}_4^+$
						3040 s	
2930 s	2950 s	2920 s	2895 s	2930 s	2890 s	2925 sh	
				2880 s		2850 m	
		2765 s	2758 s	2760 s	2755 s		OH stretching
2320 m		2350 m	2340 vw	2340 vw	2330 vw	2340 vw	combination
			1900 vw	1850 vw	1930 vw	1705 w	combination
1750 vw	1760 vw	1950 vw	1705 w				
1675 m	1670 m	1660 m	1615 vw	1660 m	1632 m		HOH bending and
1600 m	1600 m						$\nu_2$ of $\text{NH}_4^+$ (?)
		1510 sh	1510 sh	1510 sh	1505 sh		combination
		1482 sh					
		1475 s	1470 s	1467 sh	1470 sh		
1465 sh	1465 sh	1462 sh	1465 sh	1457 s	1460 s	1462 sh	
1445 sh	1442 s	1440 sh	1440 sh				$\nu_4$ of $\text{NH}_4^+$
1430 s		1432 s	1432 s	1430 s	1435 s	1435 s	
	1405 sh	1425 sh	1410 sh	1405 sh		1423 sh	
	1285 vw	1315 vw			1390 vw		combination
					1375 vw		
		1100 s	1095 sh	1099 s	1095 s	1115 sh	
1000 vs	1002 vs	1085 s	1083 s	1075 s	1068 s	1083 sh	
		1054 vs	1045 vs	1045 vs	1035 vs	1060 sh	$\nu_3$ of $\text{PO}_4^{3-}$
						1040 vs	
						1015 sh	
875 m	910 sh	970 vs	940 vs	950 sh	945 vs		$\nu_1$ of $\text{PO}_4^{3-}$ and
		951 s		935 vs	938 vs	975 m	$\text{H}_2\text{O}$ libration
754 m	740 s	775 m	822 m	728 m	738 m		$\text{H}_2\text{O}$ libration
695 sh							$\text{H}_2\text{O}$ libration?
		630 s	625 s	625 s	612 s	628 s	
						610 s	
568 s	572 s	584 s	565 s	560 s	558 s	580 s	$\nu_4$ of $\text{PO}_4^{3-}$
		570 s	558 sh	550 sh			
		558 s	537 sh				
						536 w	?
455 w		420 m				462 w	?
438 w						428 w	?

\* The numbering of the compounds is as given in the text. The abbreviations meaning: s - strong; m - medium; w - weak; v - very; sh - shoulder

The bands between 4000 and 400  $\text{cm}^{-1}$  in the reported spectra can be divided into phosphate bands, bands of the ammonium ion, and bands due to vibrations of the water molecules. Each of these groups of bands will be briefly discussed.

**Phosphate bands.** Of the four vibrational modes of the free phosphate ion the easiest to identify are the infrared active, triply degenerated  $\nu_3$  and  $\nu_4$  modes which are found to be around 1100 and 500  $\text{cm}^{-1}$ , respectively. Whereas in the spectra of the hexahydrates they appear as single bands (thus implying site symmetry of the phosphate ion not very different from tetrahedral), in the spectra of the monohydrates and of  $\text{ZnNH}_4\text{PO}_4$  they are both split, as a consequence of the lowered symmetry of the phosphate ion. This is further confirmed by the appearance of the  $\nu_1$  mode (forbidden under  $T_d$  symmetry) to which the sharp bands between 1000 and 900  $\text{cm}^{-1}$  in the spectra of III, VI and VII must be attributed. In the spectra of IV and V it is evidently overlapped by the strong band apparently due to libration of water. It is practically impossible to determine the location of the doubly degenerated  $\nu_2$  mode without having the spectra of the deuterated compounds.

**Ammonium bands.** The ammonium ion has also four vibrational modes, of which the easiest to locate is the triply degenerated  $\nu_1$  mode found around 1400  $\text{cm}^{-1}$ . Whereas in the spectra of the hexahydrates and of  $\text{ZnNH}_4\text{PO}_4$  this band appears as, more or less, single with shoulders on it, it is definitely split into at least two main bands in the spectra of the monohydrates. As in the case of the phosphate bands, this, indicates the departure from the tetrahedral symmetry of the ammonium ion, mainly due to the effect of the water molecules. It seems that to the  $\nu_2$  mode corresponds one of the two bands found between 1700 and 1600  $\text{cm}^{-1}$  in the spectra of the hexahydrates, although it is possible that they are both due to bending of water. The  $\nu_1$  and  $\nu_3$  modes are expected between 3200 and 3000  $\text{cm}^{-1}$  and it seems that the bands around 3200, 3000 and 2900  $\text{cm}^{-1}$  belong to these modes and/or combinations, since they are found in the spectrum of  $\text{ZnNH}_4\text{PO}_4$  as well.

**Water bands.** Two bands (around 3400 and 2750  $\text{cm}^{-1}$ ) in the spectra of the monohydrates could easily be assigned to O-H stretching of the water molecules. The situation is less clear with the other bands in the region between 3600 and 2500  $\text{cm}^{-1}$ , especially in the case of the hexahydrates.

The bands around  $1650\text{ cm}^{-1}$  are probably due to in-plane bending of water, whereas the bands between  $1000$  and  $600\text{ cm}^{-1}$  (with exception of  $\nu_1$  mode of the phosphate ion, being already discussed) belong, to librations of water.

On the basis of the present information it is impossible to assign all the bands with certainty. Further investigations, on the spectra of the deuterated compounds, measured at low temperatures, are in course of further investigation and will be reported later.

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Received August 14, 1967

[1] D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, 1954, 495.

[2] J. J. Étienne and A. Boullé, *Compt. Rend.*, 264, 1593 (1967).