The Infra-red Spectra of Inorganic Phosphorus Compounds. Part II. Some Salts of Phosphorus Oxy-acids.*

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The infra-red spectra of 61 salts of phosphorus oxy-acids have been examined in the rock-salt region, and general absorption regions characteristic of each class of anion are tabulated. Correlations are suggested for P–F, P–OH, PO_3^{2-}, $P-CH_3$ and other structural groupings. Previous frequency assignments have received additional confirmation and the relation of absorption to structure in these compounds is discussed.

IN Part I * the spectra of a number of inorganic salts of phosphorus oxy-acids were recorded as dry powders in the rock-salt region. The absorption bands lay in a number of regions, characteristic of each type of anion and several correlations with structural groupings were suggested. This work has now been extended and further correlations of absorption with molecular structure have been made.

EXPERIMENTAL

All spectra were recorded on a Perkin–Elmer 21C Double-beam Spectrometer. The phosphate salts were examined as dry powders spread on rock-salt plates, the techniques and conditions previously described (Part I, *loc. cit.*) being used.

RESULTS AND DISCUSSION

In Table 1 the principal regions of absorption characteristic of each type of ion are listed, together with the results from Part I. These regions are based only on the compounds examined, and a survey of a larger number of salts might in some cases necessitate slight extension of the frequency coverages. The absorption spectra of the anions may be affected by crystal-structure environment, the nature of the positive ions, hydrogen-bonded water, interaction with lattice frequencies, etc. (Part I, *loc. cit.*). In view of this, salt-by-salt comparison is liable to be less significant than the general absorption regions characteristic of each class of anions as a whole.

The Figure shows some typical spectra given by the present series of salts. The hydrated salts all absorb near 3300 and 1640 cm.$^{-1}$ which can be ascribed to the O–H stretching and bending vibrations of the water of crystallisation. Some characteristics of the spectra of the oxy-ions below 1500 cm.$^{-1}$ are as follows and a full list is given in Table 3 :

Phosphorofluoridates (*monofluorophosphates*) (I).

1210—1120 cm.$^{-1}$: a very strong broad peak (sometimes an additional strong peak at 1210—1070 cm.$^{-1}$).

1022—990 cm.$^{-1}$: a strong or medium absorption—one or two peaks.

832—721 cm.$^{-1}$: a broad absorption, sometimes resolved into two peaks.

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* Part I, *J.*, 1954, 493.

Hypophosphates (II).

1143—1040 cm $^{-1}$: several strong absorptions
931—892 cm. $^{-1}$: a strong peak, sometimes resolved into a doublet.
848—832 cm. $^{-1}$: a weak absorption in some salts.

Dihydrogen hypophosphates (III).

1270—1240 cm. $^{-1}$: a single peak of fairly strong intensity.
1151—1042 cm. $^{-1}$: several strong peaks.
928—915 cm. $^{-1}$: medium absorptions.
870—869 cm. $^{-1}$: a weak absorption.

Methylphosphonates (IV).

1430—1420 cm. $^{-1}$: a very weak absorption.
1323—1300 cm. $^{-1}$: a sharp peak of medium or strong intensity.
1124—1030 cm. $^{-1}$: a very strong absorption consisting of at least two peaks.
1000—964 cm. $^{-1}$: a strong absorption—single peak or close doublet.
877—818 cm. $^{-1}$: a medium or weak absorption.
768—758 cm. $^{-1}$: a fairly strong absorption.
730—704 cm. $^{-1}$: absorption in some salts.

Dimethylphosphinates (V).

1430—1420 cm. $^{-1}$: a very weak but distinct absorption, stronger than in the monomethyl salts.
1310—1290 cm. $^{-1}$: a medium strong peak, in some cases a doublet.
1170—1130 cm. $^{-1}$: a very strong peak.
1070—1025 cm. $^{-1}$: a very strong peak.
872—852 cm. $^{-1}$: a strong or medium absorption.
740—725 cm. $^{-1}$: a medium strong absorption.

Phosphoromonothioates (VI). Well-defined spectra were not given by these salts, which were difficult to obtain pure because of decomposition, but the absorptions appear to fall into four regions:

1110—1010 cm. $^{-1}$: the strongest absorption consisting of a single broad peak. (Some other bands up to 1135 cm. $^{-1}$ in some salts.)
990—970 cm. $^{-1}$: a strong or medium absorption.
$\left.\begin{array}{l}\text{955—935 cm.}^{-1}\\ \text{870—850 cm.}^{-1}\end{array}\right\}$: peaks of variable intensity, but usually weak, owing possibly to impurities.

Peroxydiphosphates (VII).

1157—1070 cm. $^{-1}$: the strongest absorption, usually a single broad peak.
1000—980 cm. $^{-1}$: a single strong peak.
767—720 cm. $^{-1}$: a very broad absorption of variable intensity.

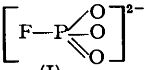
Phosphonitrilates (VIII).—The positions of some of the general absorption regions occur in a similar sequence to those of the cyclic metaphosphates (Table 1). The powder spectra of the triphosphonitrilates and the tetraphosphonitrilates are not generally sufficiently different for them to be recognised as such, although a particular metal salt should be capable of recognition from its spectrum. The absorptions are classified as follows:

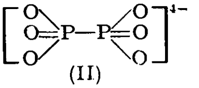
Triphosphonitrilates.

1351—1299 cm. $^{-1}$: a medium strong peak.
1223—1190 cm. $^{-1}$: a strong absorption, usually one peak.
1125—1106 cm. $^{-1}$: a weak peak.
1060—1040 cm. $^{-1}$: a very strong peak.
960—940 cm. $^{-1}$: a strong broad absorption.
850—798 cm. $^{-1}$: a weak broad absorption.

Tetraphosphonitrilates.

1375—1329 cm.$^{-1}$: a medium strong peak (in some cases two).
1220—1163 cm.$^{-1}$: a strong absorption, usually a single peak.
1115—1090 cm.$^{-1}$: a weak peak.
1062—1050 cm.$^{-1}$: a very strong peak.
970—952 cm.$^{-1}$: a strong broad absorption.
910—898 cm.$^{-1}$: medium or weak absorption.
807—788 cm.$^{-1}$: usually medium absorption.


(I)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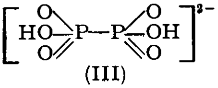
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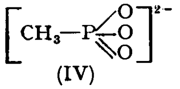
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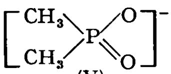
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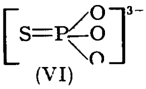
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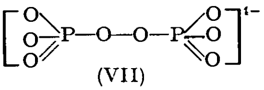
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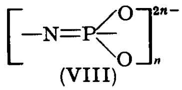
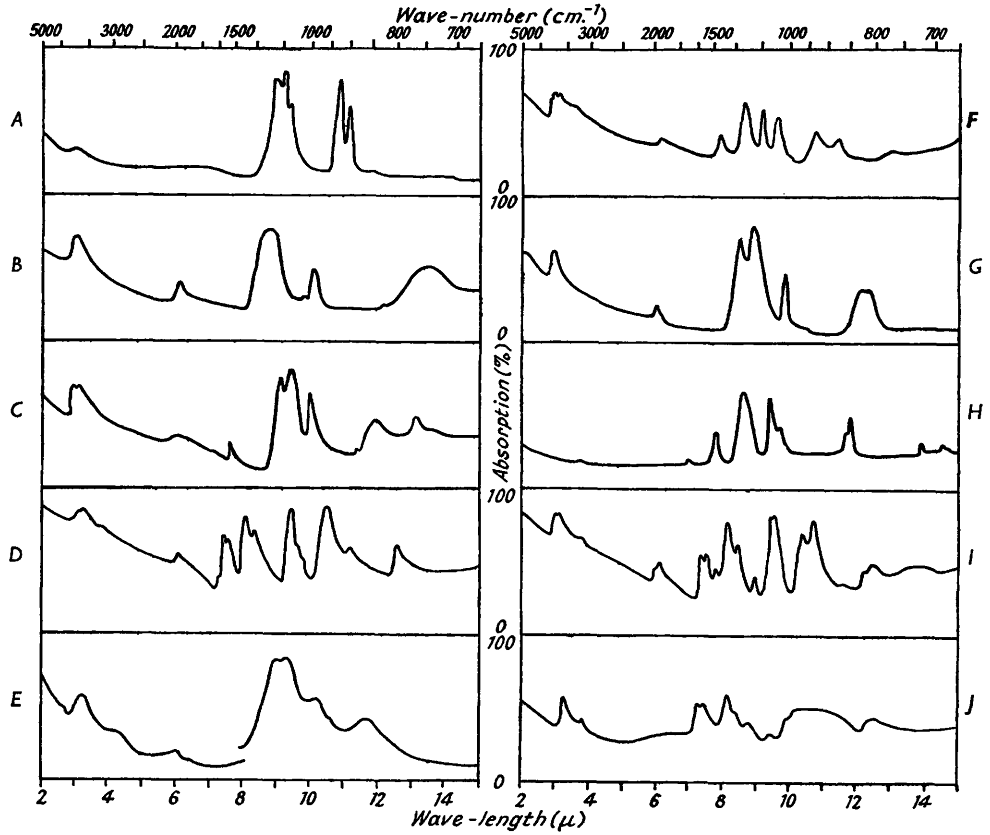

(VIII)



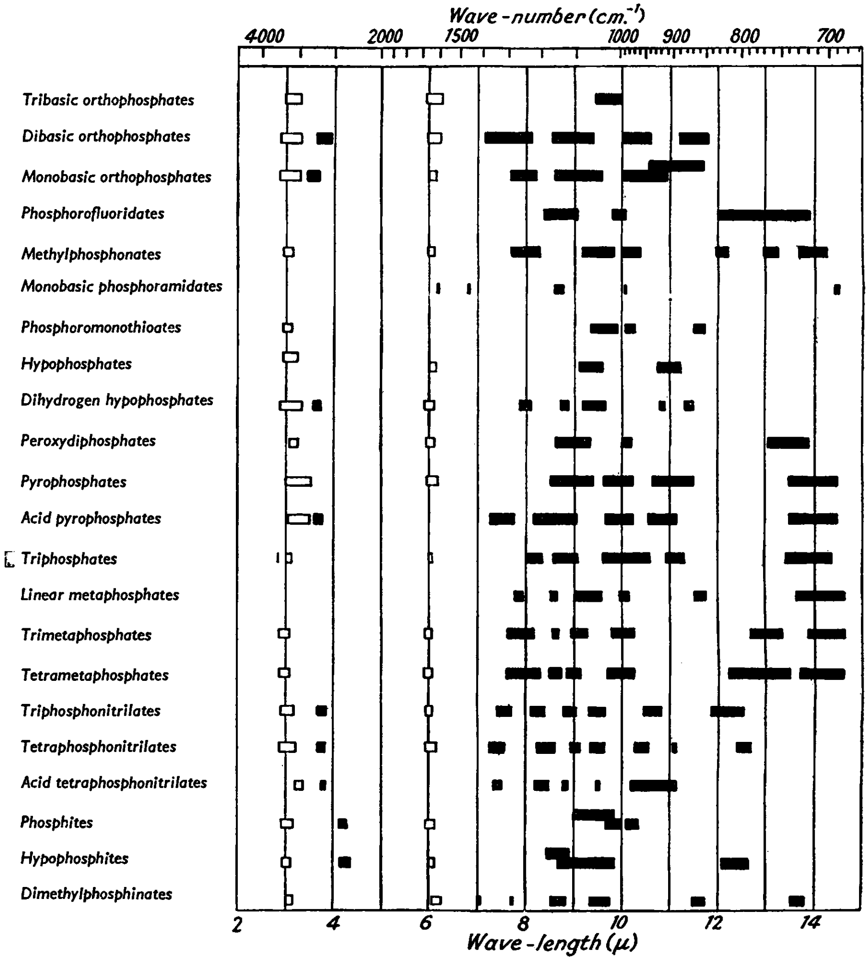
A, $Ba_2P_2O_6$; *B*, $Ca_2H_2O_8,xH_2O$; *C*, $SrPO_3Me,2H_2O$; *D*, $P_4N_4(OH)_4(ONa)_4,2{\cdot}5H_2O$; *E*, $NaBaPSO_3,8H_2O$; *F*, $Na_2H_2P_2O_6,xH_2O$; *G*, $SrPO_3F,xH_2O$; *H*, Me_2PO_2Na; *I*, $P_3N_3(OH)_3(ONa)_3,4H_2O$; *J*, $P_4N_4(OH)_6(OK)_2$.

The absorption spectra of the anhydrous acid tetraphosphonitrilates are roughly similar to those of the basic salts (Table 1). A noteworthy difference, however, is in the region of 1360—1355 cm.$^{-1}$ which contains a strong doublet in all cases. At higher frequencies the absorption near 2650 cm.$^{-1}$, although weak, is more distinct and stronger than the corresponding absorption in the more basic salts.

In Table 2 are given suggested assignments of the characteristic absorption bands to the various structural features of the oxy-acids. A discussion of these follows.

P–O *Linkages.*—The ionic phosphate vibration has already been connected with absorption at 1040—1000 cm.$^{-1}$ (Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397), 1110—1050 cm.$^{-1}$ (Bellamy and Beecher, *J.*, 1952, 1701), and 1170—1000 cm.$^{-1}$ (Corbridge and Lowe, *loc. cit.*). In the present series of compounds, all anions containing P–O linkages are again found to give very strong absorption in this region. The difference in position of the ionic phosphate absorption bands of the phosphorofluoridates and the methylphosphonates is interesting and is probably connected with the large difference in electronegativity of the attached fluorine and methyl groups in each case.

TABLE 1. *Principal absorption regions in salts of phosphorus oxy-acids.*



Unfilled rectangles denote absorption in hydrated salts only.

The effect of an increase of the electronegativity of the substituent groups leading to an increase of the P=O stretching frequency in organophosphorus compounds has been noted by Daasch and Smith (*Analyt. Chem.*, 1950, **23**, 853). The ionic phosphate bands of the phosphoramidate and peroxydiphosphate ions are at higher frequencies than those of the phosphite and phosphoromonothioate ions (Table 1), but more extended correlations may be misleading owing to complicating effects of crystal structure. The position of the ionic phosphate bands may be reflected in variations of the P–O bond lengths between different classes of anion, but no accurate bond-length data are available for comparison in compounds of this type. Bellamy and Beecher (*J.*, 1953, 728) note that the ionic phosphate bands in certain aliphatic salts occur at higher frequencies than those given by aromatic salts, which they associate with electronegativity differences.

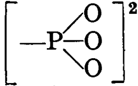
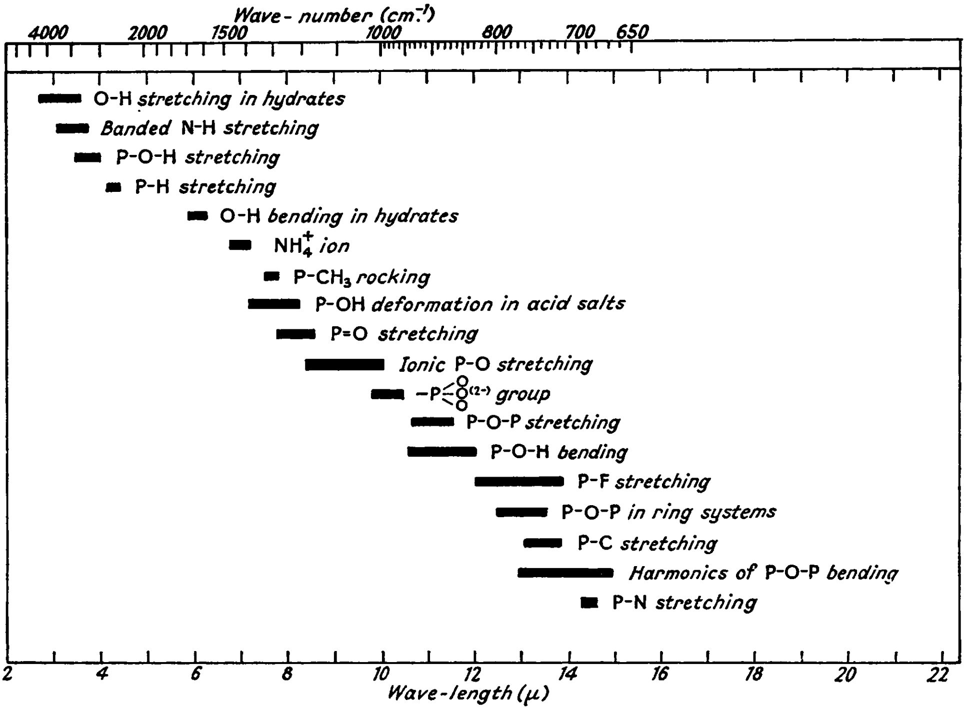
The 
$\left[-P(O)_3\right]^{2-}$
Group.—In Part I (*loc. cit.*) it was suggested that the symmetrical stretching of the P–O linkages in this group might account for the absorption observed near 980 cm.$^{-1}$ in the phosphite and phosphoramidate ions. Bands at about 1030 and 980 cm.$^{-1}$ in trialkyl phosphate have been attributed to antisymmetrical and symmetrical stretching of the three P–OR bonds (Bergmann, Littauer, and Pinchas, *J.*, 1952, 847). In more recent studies, however, Bellamy and Beecher, 1953 (*loc. cit.*) attribute these two absorptions to O–C and P–O stretching in the P–O–C linkage.

TABLE 2. *Suggested characteristic absorption bands.*



In the present series of compounds containing no P–O–C linkages, a distinct absorption appears at 1022—990 cm.$^{-1}$ in the phosphorofluoridates, 1000—964 cm.$^{-1}$ in the methylphosphonates, 1000—980 cm.$^{-1}$ in the peroxydiphosphates, and at 990—970 cm.$^{-1}$ in the phosphoromonothioates. This absorption, which appears to be associated with the $-PO_3$ grouping, is generally of medium or strong intensity and sometimes split into a close doublet, but is always weaker than the main ionic phosphate band at higher frequencies. The same characteristic absorption is noticeably absent from the hypophosphites, the dimethylphosphinates, and ammonium phosphorodifluoridate (see Table 3).

P–OH *linkages.*—A very weak, broad absorption is produced by most of the acid hypophosphate and the tri- and tetra-phosphonitrilates near 2700 cm.$^{-1}$. This we assign to P–O–H stretching and is in accordance with results reported previously (Part I, *loc. cit.*) for acid salts.

Absorption due to P–O–H bending has been ascribed to the 1050—850 cm.$^{-1}$ region (Bellamy and Beecher, *loc. cit.*, 1953) and all anions containing such a group are observed to absorb here, although this absorption could be due to other causes (Part I, *loc. cit.*).

Characteristic of the acid phosphate ions are medium or strong absorptions at about 1400—1220 cm.$^{-1}$ (cf. acid hypophosphates, acid pyrophosphates, and acid orthophosphates with the corresponding neutral salts). This absorption, which is most marked with the cyclic phosphonitrilates, appears to be connected with the P–OH linkage, and presumably arises from some deformation mode of this group.

P–F *Linkage.*—The absorption at 835—720 cm.$^{-1}$ found in all the phosphorofluoridates, is probably due to P–F stretching. Ammonium phosphorodifluoridate also absorbs in this region. P–F stretching has been assigned to the region 990—840 cm.$^{-1}$ in PF_3, POF_3, and PF_5 (Gerrard, *J.*, 1940, 1454; Delwaulle and Francois, *Compt. rend.*, 1947, **224**, 1422; Gutowsky and Liehr, *J. Chem. Phys.*, 1952, **20**, 1652); and 980—740 cm.$^{-1}$ in organophosphorus compounds (Daasch and Smith, *loc. cit.*).

P–CH_3 *Linkage.*—By analogy with such compounds as Me_3P and Me_3PO (Daasch and Smith, *J. Chem. Phys.*, 1951, **19**, 22), the P–C stretching vibration is to be expected in the region 750—650 cm.$^{-1}$. Daasch and Smith observed absorption near 750 cm.$^{-1}$ in a number of organophosphorus compounds containing P–C links, but owing to interfering absorptions were not able to make a decisive assignment. The methylphosphonate absorptions at 768—758 cm.$^{-1}$ and the dimethylphosphinate absorptions at 740—725 cm.$^{-1}$ are probably connected with P–C stretching. The other absorptions, at 877—818 cm.$^{-1}$ in the monomethyl salts and at 872—852 cm.$^{-1}$ in dimethyl salts, may be connected with C–H rocking.

No strong bands are given by the methylphosphonates in the 2900—2800-cm.$^{-1}$ region in which C–H stretching absorptions usually appear. Absorptions connected with water vibrations occur at 3450—3150 cm.$^{-1}$ in these salts, but no shoulder bands are evident in the adjacent methyl C–H stretching region and this absorption must therefore be very weak. In the methyl C–H bending region near 1380 cm.$^{-1}$ only very weak inflexions are evident on the methylphosphonate absorption curves, but a distinct, although very weak, absorption is found near 1420 cm.$^{-1}$ in the dimethylphosphinates.

It may be inferred that the reduction of intensity of these absorptions is associated with a weakening of the methyl group dipole induced by the attachment to phosphorus. Wright and Hunter (*J. Amer. Chem. Soc.*, 1947, **69**, 803) noticed a similar effect with Si–CH_3 groups where the C–H bending and stretching absorptions were reduced to about one quarter of the intensity usually observed when the methyl group is attached to carbon.

The sharp absorption (sometimes a doublet) near 1320 cm.$^{-1}$ we attribute to the phosphorus–methyl rocking vibration. This may be compared with the rocking frequency near 1260 cm.$^{-1}$ in the Si–CH_3 group (Wright and Hunter, *loc. cit.*) and near 1250 cm.$^{-1}$ in the C–CH_3 group (Torkington, *J. Chem. Phys.*, 1950, **18**, 768). Like the Si–CH_3 rocking absorption, that of P–CH_3 is stronger than that given by C–CH_3, moreover the absorption due to P–C stretching is also fairly intense. These facts indicate a relatively strong dipole moment of the P–CH_3 linkage. The presence of such a dipole might account for the observed weakening of the C–H vibrations of the methyl groups.

Phosphonitrilates.—The phosphonitrilates all give strong bands at 1400—1220 cm.$^{-1}$ and in most cases a weak absorption is found near 2700 cm.$^{-1}$. These absorptions have already been associated with P–OH groups and their appearance may be an indication of formula (IX*a*) rather than (IX*b*) (Audrieth, Steinman, and Toy, *Chem. Reviews*, 1943, **82**, 109) for the constitution of anions of this type. The more pronounced P–OH stretching and deformation bands observed in the isomorphous acid tetraphosphonitrilates (Corbridge, *Acta Cryst.*, 1953, **6**, 104) may be associated with the extra hydroxyl groups present in this anion (IX*c*).

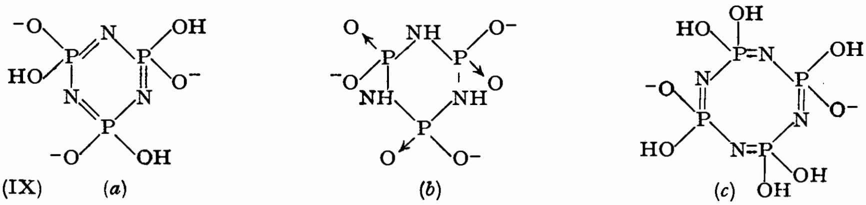

(IX) (*a*) (*b*) (*c*)

TABLE 3. *Positions and intensities of infra-red absorption bands.*

Phosphorofluoridates

(1) $NH_4PO_2F_2$
2900—2550 mw, bv
1445 w, sh
1414 s
1262 s
1125 s
1005 vvw
870 w, sh
832 s

(2) $(NH_4)_2PO_3F,H_2O$
~2600 w, vb
1430 s, b
1370 w, sh
1170 w, sh
1138 s
1070 s
990 ms
755 s

(3) $Li_2PO_3F,3H_2O$
3330 m
1635 mw
1160 s
1120 s
1020 mw
832 mw, b

(4) Na_2PO_3F
~1205 vw, sh
1170 s
1019 w, sh
1010 mw
763 m, b
721 m

(5) K_2PO_3F
1210 vw, sh
1166 s
1013 ms
738 m, b

(6) $CaPO_3F,xH_2O$
3500 m
3030 m
1640 mw
1160 vs
1018 s
797 ms

(7) $SrPO_3F,xH_2O$
3340 m
1655 mw
1182 s
1120 vs
1022 m
823 m
808 m

(8) $BaPO_3F$
1163 s
1127 vs
1005 ms
~ 745 m, b

(9) $PbPO_3F$
~1110 vb, vs
~1000 vw, sh
990 m
~ 783 m, b

(10) Ag_2PO_3F
1210 w, sh
1162 s
1018 w, sh
1010 m
760—720 m, vb

Hypophosphates

(11) $Na_4P_2O_6,10H_2O$
3320 vw, sh
3140 m
2990 m
1645 w
1125 vw, sh
1062 vs
916 s

(12) $K_2Na_2P_2O_6,10H_2O$
3275 mw, sh
2980 ms
1660 w, b
1103 vw, sh
1080 m, sh
1050 vs
911 s
832 w
~ 750 vw

(13) $Ca_2P_2O_6,2H_2O$
~3100 m, b
1640 w, b
1135 vw, sh
~1090 vs, b
1020 vw, sh
922 s
~ 860 vw, b

(14) $Sr_2P_2O_6,2H_2O$
3360 m, b
1640 w, b
1136 vw, sh
1103 vs
1075 s
~1020 vw, sh
978 vw
931 s
922 s
~ 848 vw, b

(15) $Ba_2P_2O_6$
1112 m
1090 vs
1061 w, sh
1028 vw
1009 vvw
954 vvw
921 s
905 s

(16) $Pb_2P_2O_6$
~1076 m, b
1040 s, b
892 ms

Dihydrogen hypophosphates

(17) $(NH_4)_2H_2P_2O_6$
~3200 w, sh
2970 m
2880 m
2775 m
1845 w
1680 m
1559 vw
1541 vw
1480 m
1455 w
1414 m
1240 ms
1128 vs
1043 vs
969 s
915 s
870 vw, sh
694 vw

(18) $Na_2H_2P_2O_6,xH_2O$
3490 w
3360 m
3250 w
2780 w
1652 w
1270 ms
1151 s
1094 ms
1042 ms
928 m
869 mw
764 vw, b

(19) $Rb_2H_2P_2O_6,xH_2O$
3460 w, sh
3350 m
3230 w
~2760 vw
1645 mw
1266 ms
1149 s
1092 ms
1046 m
994 m
927 mw
869 mw
845 vw, sh

Methylphosphonates

(20) $Na_2PO_3Me,6H_2O$
3230 m, b
1645 w
1426 vvw
1310 w
~1062 vs
1035 s
973 s
831 m, b
757 ms
702 ms, vb

(21) $MgPO_3Me$
1425 vvw
1310 mw
1102 s
1016 s
985 vw, sh
770 m, b

TABLE 3. (*Continued.*)

(22) $CaPO_3Me,2H_2O$
~3350 vw, sh
3250 mw
1670 mw
1420 vvw
1323 mw
1124 vw, sh
1100 s
1030 vs
987 m
877 vw
768 m, s

(23) $SrPO_3Me,2H_2O$
3400 vw, sh
3175 m, b
1640 vw, b
1428 vvw
1308 w
1091 s
1052 s
1000 m
876 vw
837 m, b
764 m

(24) $BaPO_3Me$
1421 vvw
1302 mw
1115 w, sh
1087 w, sh
1053 vs
977 s
~859 vw, vb
759 m, s

(25) Ag_2PO_3Me
3330 m
3175 m
1670 vw
1430 vvw
1315 w
1307 w
1055 vs
1037 m, sh
1008 m, sh
977 vw, sh
968 s
835 w, b
760 ms
704 m, b

(26) $PbPO_3Me$
1420 vvw
1300 w
1057 s
993 s
964 s
763 m
758 m

Dimethylphosphinates

(27) $LiPO_2Me_2$
~1420 w
1309 m
1290 vw
1048 s
1026 s
971 vw
922 mw
871 ms
740 ms
698 vw

(28) $NaPO_2Me_2$
1420 w
1295 m
1168 s
1068 s
1028 w
862 vw
852 m
725 m
695 vw

(29) KPO_2Me_2,xH_2O
3200 s
2911 vw, sh
1633 m, b
1422 w
1292 ms
1153 vs
1048 s
918 m, b
856 s
778 w, b
722 m, b
~687 vw, vb

(30) $Ca(PO_2Me_2)_2,xH_2O$
~3030 w, b
1605 w, b
1419 w
1294 m
1131 s
1041 s
973 vw, b
917 w, b
862 m
738 vw, b

(31) $Sr(PO_2Me_2)_2,xH_2O$
~3270 s
1650 w, b
1420 w
1297 m
1120 s
1040 s
990 m
~935 vw, sh
863 ms
769 m
737 m

(32) $Ba(PO_2Me_2)_2,xH_2O$
~3200 mw, vb
~1625 w, b
1420 w
1291 ms
1130 vs
1044 vs
975 w, b
915 w, b
861 s
810 w, b
753 vw, sh
735 m

Phosphoromonothioate

(33) $Na_3PSO_3,10H_2O$
3430 s
1642 mw
1252 w
~1157 ms
~1125 ms
1068 s
988 vw
952 ms
860 ms

(34) $NaCaPSO_3,8H_2O$
~3040 m, b
~1640 w
1101 m, sh
~1030 s, b
~ 952 w, sh
~ 865 w, b

(35) $NaSrPSO_3,8H_2O$
~3140 m, b
~1620 vw
1262 w, b
1135 m, sh
1053 s
1006 s
~844 w, b

(36) $NaBaPSO_3,8H_2O$
~3080 m, b
~1650 w, b
1240 vw, b
~1143 w, sh
1104 s
1073 s
984 m, w
854 m, b

(37) $Co_3(PSO_3)_2$
~3250 m, b
~1608 w, b
~1080 s
~1038 s
~ 990 s
~ 897 vw, vb

(38) $Ni_3(PSO_3)_2$
3360 m
2900 w, sh
~1636 w, b
1117 w, sh
~1040 s, b
~ 889 w, b
~855 w, b

(39) $Pb_3(PSO_3)_2$
1610 vw
1018 s, b
960 w, sh
924 w
~874 vw, sh

TABLE 3. (*Continued.*)

Peroxydiphosphates

(40) $Li_4P_2O_8,xH_2O$
- 3220 ms, b
- 1640 w
- 1115 s
- 1070 vs
- 998 s
- 767 w, vb

(41) $Na_4P_2O_8,xH_2O$
- 3100 ms, b
- 1640 w
- 1115 m, sh
- 1075 s
- 1000 s
- ~735 w, vb

(42) $K_4P_2O_8,xH_2O$
- 3270 ms, b
- 1680 w
- 1655 w
- 1185 m, sh
- 1157 s
- 1135 s
- 1094 w, sh
- 995 m
- 980 m
- 790 vw, sh
- 720 s, vb

(43) $Ca_2P_2O_8,xH_2O$
- 3250 m, b
- 1640 w
- 1140 s, b
- 991 m
- 815 vw
- 743 m, vb

(44) $Sr_2P_2O_8,xH_2O$
- 3350 m, b
- 1640 w
- 1140 s, b
- 986 m
- 732 m, vb

(45) $Ba_2P_2O_8,xH_2O$
- 3250 m, b
- 1640 w
- 1140 s, b
- 980 m
- 730 m, vb

Triphosphonitrilates

(46) $P_3N_3(OH)_3(ONa)_3,4H_2O$
- 3300 m, b
- 3175 vw
- 2690 vvw
- 1640 w
- 1351 m
- 1322 m
- 1279 w
- 1223 s
- 1190 w
- 1118 w
- 1062 s
- 1053 s
- 958 m
- 929 s
- 856 vw
- 817 w
- 798 m
- 728 w, vb

(47) $P_3N_3(OH)_3(ONa)(O_2Mg),6H_2O$
- 3175 m, b
- 2690 v, w
- 1645 w
- 1310 m
- 1210 s
- 1125 vw
- 1059 s
- 950 s, b
- 823 vw, b

(48) $P_3N_3(OH)_3(ONa)(O_2Ca),4H_2O$
- 3200 m, b
- 2630 vvw
- 1635 w
- 1317 ms
- 1200 s, b
- 1116 w
- 1056 s
- 952 s, b
- 847 w, b

(49) $P_3N_3(OH)_3(ONa)(O_2Sr),4H_2O$
- 3230 m, b
- 2620 vvw
- 1640 w
- 1310 ms
- 1209 s
- 1110 w
- 1057 s
- 944 s, b
- ~820 vw, vb

(50) $P_3N_3(OH)_3(ONa)(O_2Ba),1{\cdot}5H_2O$
- 3150 m, b
- 2660 vvw
- 1632 w, b
- 1311 ms
- 1198 s
- 1106 w
- 1051 s
- 940 s, b
- 823 w, b

(51) $P_3N_3(OH)_3(OAg)_3$
- 1338 m
- 1299 w
- 1192 s
- 1140 vw
- 1100 vw
- 1040 s
- 960 s
- 926 s
- 826 w, b
- 787 vw, b

Tetraphosphonitrilates

(52) $P_4N_4(OH)_6(ONH_4)_2$
- 3125 m, b
- 2750 vvw
- 1635 vw
- 1440 vw, sh
- 1404 m
- 1360 vw, sh
- 1335 m
- 1215 vw, sh
- 1190 s
- 1137 m
- 1057 s
- 950 s, b
- 893 w, sh
- 785 vw, b

(53) $P_4N_4(OH)_6(OK)_2$
- 3020 m
- 2650 w
- ~1650 vw, vb
- 1358 m
- 1340 m
- 1215 s
- 1182 vw
- 1140 w
- 1060 w
- 1002 vw, sh
- 980—900 m, vb
- 804 w, b

(54) $P_4N_4(OH)_6(ORb)_2$
- 3000 m
- 2630 w
- ~1620 vw, vb
- 1358 m
- 1340 m
- 1210 s
- 1140 vw
- 1061 vw
- 974 m, sh
- 891 s, vb
- 790 w, vb

(55) $P_4N_4(OH)_4(ONa)_4,2{\cdot}5H_2O$
- 3280 w
- 3115 w
- 2625 vvw
- 1637 w
- 1375 vw, sh
- 1349 m
- 1329 w, sh
- 1220 s
- 1187 w
- 1061 s
- 1041 vw, sh
- 1027 w, sh
- 959 vs, b
- 898 w, b
- 789 m

(56) $P_4N_4(OH)_4(O_2Ca)_2,4H_2O$
- 3350 vw, sh
- 3110 w
- 2600 vvw
- 1620 w
- 1338 s
- 1206 vs
- 1178 s
- 1058 ms
- 969 vs, b
- 897 w, vb
- 798 m

(57) $P_4N_4(OH)_4(O_2Ba)_2,2H_2O$
- 3400 w, sh
- 3200 m
- 2640 vvw
- 1650 vw
- 1332 s
- 1184 vs
- 1104 vw
- 1068 w, sh
- 1058 s
- 1025 m
- 970 vs
- 883 w, b
- 796 m

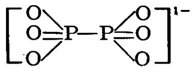
TABLE 3. (*Continued.*)

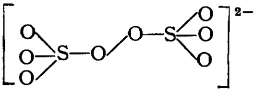
(58) $P_4N_4(OH)_4(OAg)_4$	(59) $P_4N_4(OH)_4(O_2Cu)_2,4H_2O$	(60) $P_4N_4(OH)_4(O_2Ni)_2,2\cdot5H_2O$
1387 mw	3390 m	3140 m, b
1337 m	3300 vw	2670 vvw
1164 s	3210 w	1640 mw
1127 m	3080 mw	1335 s
1052 m	2735 w	1188 s
1030 vw	1651 mw	1110 vw
1000 ms	1389 m	1059 m
947 s, b	1370 vw	1018 vw, sh
816 m, b	1293 s	976 vs, b
760 w, vb	1206 m	955 w, sh
710 m, vb	1177 vs	910 w, b
	1158 vw	802 w, b
	1147 vw	
	1118 vw	(61) $P_4N_4(OH)_4(O_2Pb)_2,xH_2O$
	1092 w	3150 w, b
	1069 w	2645 vvw
	1035 m	1625 vw
	990 vw, sh	1335 s
	952 s	1163 s, b
	898 w	1096 vw
	807 m	1050 m
	792 vw, vb	980 ms
	705 w, b	964 s
		900 vw, b
		788 m, b

The spectra of the parent chlorides (Daasch and Smith, *loc. cit.*) contain only two strong absorptions in the rock-salt region at about 1300—1250 and 900—850 cm.$^{-1}$. Since stretching absorptions involving the P–Cl linkages should occur at much lower frequencies (Daasch and Smith, *loc. cit.*), these two strong absorptions are probably connected with the ring structure which has been shown to be present by crystal-structure measurements (Ketelaar and de Vries, *Rec. Trav. chim.*, 1939, **58**, 1081). The strong absorptions observed near 1200 and 900 cm.$^{-1}$ in the phosphonitrilate salts may arise from similar causes.

Miscellaneous Bands.—Since the symmetrical formula (X) is now regarded as established for the hypophosphate ion (Raistrick and Hobbs, *Nature*, 1949, **164**, 113), the absorption found at 931—892 cm.$^{-1}$ in the spectra of the hypophosphates is unlikely to be due to P–P stretching and cannot arise from P–O–P stretching. This absorption is more likely due to stretching of the $-PO_3$ group, which has been shifted to lower frequencies than usual, by the adjacent phosphorus atom.

(X)





(XI)

In the spectra of the peroxydiphosphates, the absence of absorption in the P–O–P stretching region is in accordance with the structural formula usually assumed for the peroxydiphosphate ion. The geometrical configuration of this ion, which may resemble that found (XI) for the peroxydisulphate ion (Zachariarsen and Mooney, *Z. Krist.*, 1934, **88**, 63), has not yet been determined from crystal structure measurements, and assignment of the absorption at 767—720 cm.$^{-1}$ is rendered somewhat speculative.

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