212. *Studies of Phosphates. Part III. Some Complex Orthophosphates of Sodium and a Bivalent Metal, and Some Orthophosphate Solid Solutions.*

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The action of sodium phosphate on solutions of salts of those bivalent metals with which the present paper deals is no doubt essentially similar to that of ammonium or potassium phosphates. Owing to the greater solubility imparted by the sodium, and the tendency of the latter to form hydrated ions, compounds can, however, be obtained by its use, which either have no counterpart or are at least more difficult to obtain when using the other two phosphates. Some of these compounds are peculiar, and raise considerable difficulties, owing to a marked tendency for solid solutions to be formed. All of them are well crystallised.

Nickel and zinc chloride solutions in the cold yielded respectively $NaNiPO_4,7H_2O$ and a compound which approximates to $NaZnPO_4,H_2O$, and from hot solutions the anhydrous zinc and cadmium analogues were obtained (Expt. A). The last two compounds had been prepared by Ouvrard (*Ann. Chim. Phys.*, 1889, **16**, 289; *Compt. rend.*, 1888, **106**, 1729) by fusion of sodium phosphate with the metallic oxide.

Magnesium chloride from hot solution yielded square prisms of a new *compound* $Na_3MgH(PO_4)_2$ or $NaMgPO_4,Na_2HPO_4$ (Expt. B). By the action of magnesia in the cold on sodium dihydrogen phosphate solution, Schröcker and Violet (*Annalen*, 1866, **140**, 229) obtained the compound $NaMgPO_4,9H_2O$. Manganese gave small plates of a *compound* corresponding closely to the formula $Na_3MnH(PO_4)_2$, but differing sufficiently to show that this formula did not give a correct representation of the substance. The several preparations could be represented as solid solutions of varying compositions based on the two constituents $NaMnPO_4$ and Na_2HPO_4 (Expt. C).

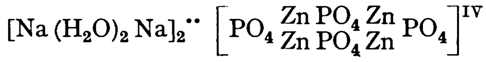
Copper gave rosettes of nearly rectangular greenish-blue plates, which could be represented very closely by a formula $5NaCuPO_4,2Na_2HPO_4$. Cadmium gave acicular crystals of composition, in different preparations, ranging from $5NaCdPO_4,Na_2HPO_4$ to $7NaCdPO_4,Na_2HPO_4$. Cobalt yielded purplish-blue, nearly square prisms, which corresponded to the formula $2Na_2HPO_4,Co_3(PO_4)_2,8H_2O$ (Expt. D). None of the above curious *compounds* of magnesium, manganese, copper or cadmium appears to have been obtained before, but the *sodium nickel* and the *sodium cobalt* compound were prepared by Debray (*Compt. rend.*, 1864, **59**, 40; *Bull. Soc. chim.*, 1864, **3**, 11), who gave no details of the preparation and no analysis.

The green colour of $NaNiPO_4,7H_2O$ indicates that the nickel is entirely kationic. The difference in the degree of hydration of the sodium and the potassium salts (see Part I, p. 857) is undoubtedly due to the much greater tendency for the sodium ion to be hydrated. We know of no statistical evidence to suggest that the phosphate ion ever carries a water molecule in the same way as the sulphate ion does. There is reason for supposing that a monohydrated sodium ion is unstable with respect to an ion $[Na(H_2O)_2Na]^{\cdot\cdot}$, in which the two water molecules are shared (Bassett and Sanderson, J., 1932, 1855). For the above reasons the most likely structure for the compound appears to be that shown in Table I. On ignition, this passes into

$$Na_4^{\cdot}\left[PO_4\begin{matrix}Ni\,PO_4\,Ni\\Ni\,PO_4\,Ni\end{matrix}PO_4\right]^{''''}$$

with the same brown anion which is present in the ignited " glowed " $[Ni_3(PO_4)_2]_2$ (Part II, p. 873). We have not been able to detect any " glowing on ignition," presumably because loss of water and polymerisation occur at too low a temperature.

The structure of $NaZnPO_4,H_2O$ is at present uncertain. We suggest



$$[Na\,(H_2O)_2\,Na]_2^{\cdot\cdot}\left[PO_4\begin{matrix}Zn\,PO_4\,Zn\\Zn\,PO_4\,Zn\end{matrix}PO_4\right]^{IV}$$

rather than the structure assigned to $(NH_4ZnPO_4,H_2O)_4$ (Part I, Table I) because (*a*) the crystal forms are quite different and (*b*) the sodium salt is much more stable than the ammonium salt; at ordinary temperatures it appears to have no tendency to lose its water.

The crystalline form of the anhydrous sodium zinc and cadmium phosphates appears to be rather different from that of the potassium compounds (Part I, p. 868). Neither of them glows on ignition, but owing to the ease with which they melt, this is of no diagnostic value.

The compound $Na_3MgH(PO_4)_2$ was formed under sufficiently varied conditions to establish its definite entity. It is well crystallised, as are the compounds $NaZnPO_4$ and $NaCdPO_4$ and also the solid solutions containing manganese, copper, or cadmium, which can be written $xNaMPO_4,yNa_2HPO_4$. In their mode of origin all these substances appear to be closely related, and, after carefully considering other possibilities, we have come to the conclusion that the magnesium salt is best formulated as in Table I.

TABLE I.

Type of phosphate.	Structural formulæ assigned by us.	Metals yielding this type of compound. (New compounds in italics.)	Colour of the phosphate.	Behaviour on ignition.*
$NaMPO_4,7H_2O$	$[Na(H_2O)_2Na]^{\cdot\cdot}[M(H_2O)_6]_2^{\cdot\cdot}[PO_4]_2'''$	Nickel	Green	N.-g.
$Na_3MH(PO_4)_2$	$Na_6^{\cdot}\left[PO_4\,M\,PO_4\genfrac{}{}{0pt}{}{H}{H}PO_4\,M\,PO_4\right]^{VI}$	*Magnesium*	—	†
$NaMPO_4$	$Na_4^{\cdot}\left[PO_4\genfrac{}{}{0pt}{}{M\,PO_4\,M}{M\,PO_4\,M}PO_4\right]''''$	Zinc Cadmium	— —	† †
Solid solutions	Solid solutions of	*Manganese*	White with very pale cream or pink tinge	†
$xNaMPO_4,yNa_2HPO_4$	$Na_4^{\cdot}M^{\cdot\cdot}[PO_4\,M\,PO_4\,M\,PO_4\,M\,PO_4]^{VI}$	*Copper*	Greenish-blue	†
	in $Na_4^{\cdot}\left[PO_4\,M\,PO_4\genfrac{}{}{0pt}{}{H}{H}PO_4\,M\,PO_4\right]^{VI}$	*Cadmium*	—	†
Solid solutions of $2MHPO_4,M_3(PO_4)_2,12H_2O$ and $2K_2HPO_4,M_3(PO_4)_2,4H_2O$	Solid solutions of $3[M(H_2O)_4]^{\cdot\cdot}\left[PO_4\,M\,PO_4\genfrac{}{}{0pt}{}{H}{H}PO_4\,M\,PO_4\right]^{VI}$ in $K_4'[M(H_2O)_4]^{\cdot\cdot}\left[PO_4\,M\,PO_4\genfrac{}{}{0pt}{}{H}{H}PO_4\,M\,PO_4\right]^{VI}$	*Cadmium*	—	†
$2Na_2HPO_4,M_3(PO_4)_2,8H_2O$	$4[Na(H_2O)_2]^{\cdot}M^{\cdot\cdot}\left[PO_4\,M\,PO_4\genfrac{}{}{0pt}{}{H}{H}PO_4\,M\,PO_4\right]^{VI}$	Cobalt	Purplish-blue	†
$2MHPO_4,M_3(PO_4)_2.4H_2O$	$[M(H_2O)_4]^{\cdot\cdot}M_2^{\cdot\cdot}\left[PO_4\,M\,PO_4\genfrac{}{}{0pt}{}{H}{H}PO_4\,M\,PO_4\right]^{VI}$	Manganese Cadmium	Pale yellowish-pink —	N.-g. N.-g.

* N.-g. = non-glowing; † denotes that phosphate melts at a temperature below which glowing usually occurs.

The manganese, copper, or cadmium solid solutions originate from structures corresponding to the above by simultaneous replacement of the two hydrogens and two sodium ions by the corresponding bivalent ion in the manner shown in Table I. The greenish-blue colour of the copper solid solution is in favour of the view that some of the copper is kationic and some anionic.

So long as there is a reasonable proportion of the constituent containing hydrogen present, the other constituent remains stable in the chain form, but when all hydrogen has been replaced, the bivalent metal ion becomes 4-co-ordinate, and ring closure follows with formation of

$$Na_4^{\cdot}\left[PO_4\genfrac{}{}{0pt}{}{M\,PO_4\,M}{M\,PO_4\,M}PO_4\right]''''.$$

Expt. A shows that $NaMPO_4$ or $(NaMPO_4)_4$ really is the final product of the replacement action, and the crystalline form appears to be definitely different from that of $Na_3MgH(PO_4)_2$ or the solid solutions.

Although under suitable conditions potassium cadmium phosphate monohydrate is definitely formed by interaction of potassium phosphate and cadmium chloride (Part I, Expt. F), yet products of variable composition but of well-crystallised character are obtained under other conditions (Expt. E).

These solid solutions can be formulated in a similar manner to the sodium compounds just considered, with the results shown in Table I.

The compound which is generally and conveniently written as $2Na_2HPO_4,Co_3(PO_4)_2,8H_2O$ is by far the most striking of the complex orthophosphates containing sodium. At first we were inclined to regard it as $[Na(H_2O)_2]_4^{\cdot}\,[H\,PO_4\,Co\,PO_4\,Co\,PO_4\,Co\,PO_4\,H]^{IV}$, in which all the cobalt was in the anion. Two objections can be urged against such a structure, however: first, the colour of the compound is definitely too purple for one in which the cobalt is entirely anionic, and secondly, the above structure does not emphasise the close relationship which probably exists between the blue compound and the solid solutions just previously considered. A close relationship seems indicated by the similarity in the methods by which they are obtained.

For these reasons we consider that the most likely structure for the compound is the one shown in Table I, with an anion of the same type as that already postulated for the solid solutions containing manganese, copper, and cadmium. Our reason for supposing that the whole of the water is associated with the sodium and none with the cobalt kation is mainly that the colour is not as red as would have been expected had $[Co\ (H_2O)_4]^{\bullet\bullet}$ been present (cf. Bassett and Croucher, J., 1930, 1796). We suppose the cobalt ion to have a weak colouring power in comparison with $[Co\ (H_2O)_4]^{\bullet\bullet}$. The colour is much more akin to that of the ignited normal phosphate, which we have formulated as

$$Co_2^{\bullet\bullet}\left[PO_4\begin{matrix}Co\,PO_4\,Co\\Co\,PO_4\,Co\end{matrix}PO_4\right]^{''''}$$

(Part II, p. 873).

The complex sodium salt is distinctly bluer than the ignited normal phosphate, which agrees well with the above formulæ since it would only contain one cobalt kation as compared with two in the ignited phosphate.

Phosphates of the Type $2MHPO_4,M_3(PO_4)_2,4H_2O$.—Two representatives of this interesting type of complex phosphate—the manganese and the cadmium compound—were obtained in a well-crystallised form during our experiments with pyridine mixtures (Expt. F). Both of these were previously known (Ephraim and Rossetti, *Helv. Chim. Acta*, 1929, **12**, 1025). The second appears to have been originally obtained by de Schulten (*Bull. Soc. chim.*, 1889, **1**, 472), though, in the absence of precise experimental details, we were not able to get his result (see Part II, Expt. C).

Ephraim and Rossetti's compound $2{\cdot}5CuO,P_2O_5,3H_2O$ (*loc. cit.*) may well have been slightly impure $2{\cdot}5CuO,P_2O_5,2{\cdot}5H_2O$, *i.e.*, $2CuHPO_4,Cu_3(PO_4)_2,4H_2O$, corresponding to the above manganese and cadmium compounds.

It is clear that these compounds must be given a similar structure to that assigned to the blue sodium cobalt compound and this is given in Table I, which summarises the compounds and solid solutions considered in the present paper. The structures there given are certainly not the only ones which might be put forward. They appear to us to account for all the known facts more satisfactorily than any others we have been able to devise. Our justification for proposing any structures lies in the fact that some theory is necessary to enable one to link up and correlate such complicated compounds which, though obviously closely related, are yet apparently so diverse. Complexes containing four atoms of phosphorus appear to play a very important part in the chemistry of the phosphates of bivalent metals. Crystallographic examinations of a number of the compounds dealt with in the present papers are being made and it is hoped to be able to make *X*-ray examinations also.

EXPERIMENTAL.

Bivalent metals and phosphate were determined as in Part I. Sodium in our earlier analyses was weighed as sulphate after removal of other metals and phosphate as there described. In the later analyses sodium estimations were done by the zinc uranyl acetate method, which gave excellent results. Heavy metals were removed by hydrogen sulphide, and phosphoric acid by magnesia mixture, only a small excess of the latter being used; the triple sodium salt was precipitated directly in the filtrate from the ammonium magnesium phosphate. This method saves much time and gives much better results than the earlier one, as it avoids the tedious filtration of the ferric or stannic phosphate precipitates. In the analyses of phosphates containing only magnesium, zinc, or cadmium in addition to sodium, removal of the phosphate alone was required before precipitation of the sodium.

It was essential in all cases to carry out a blank estimation with the same amounts of reagents as had been used in the main experiments.

Losses on ignition were often somewhat high owing to volatilisation of alkali (cf. Part I, p. 865).

Expt. A (*Theory, p.* 877). *Sodium Metal Phosphates,* $NaMPO_4,xH_2O$.—*Nickel* ($x = 7$). Solutions containing 50 g. of crystallised disodium hydrogen phosphate in 300 c.c. of water and 3 g. of nickel chloride hexahydrate in 50 c.c. of water were mixed at room temperature. The precipitate changed in five days to large green double pyramids. The ignited compound is brown [Found: NiO, 24·46; P_2O_5, 23·24; loss on ignition, 42·06; Na_2O (by diff.), 10·24. $NaNiPO_4,7H_2O$ requires NiO, 24·68; P_2O_5, 23·46; Na_2O, 10·24; loss, 41·63%].

Zinc ($x = 1$). Solutions containing 3·4 g. of zinc chloride in 100 c.c. of water and 50 g. of disodium hydrogen phosphate crystals were mixed and kept at room temperature, the total bulk being 600 c.c. After 23 days the precipitate formed crystalline, irregular tetrahedra, distinct from the hexagonal prisms of the anhydrous salt. The *monohydrate* appears to persist indefinitely at room temperature, though on the water-bath it is unstable with reference to the anhydrous compound. In a second preparation only half the above quantity of zinc chloride was used in a total volume of 500 c.c., the other conditions being the same [Found: ZnO, (1) 39·22, (2) 39·71; Na_2O, (1) 15·06,* (2) 14·95 †; P_2O_5, (1) 35·29, (2) 35·71; loss on ignition, (1) 11·94, (2) 11·00. $NaZnPO_4,H_2O$ requires ZnO, 40·42; Na_2O, 15·40; P_2O_5, 35·27; loss, 8·94%]. The high loss on ignition may be partly due to loss of alkali, as in other cases, but the analyses also indicate the formation of solid solutions, the constituents of which are at present uncertain.

Zinc ($x = 0$) *and cadmium* ($x = 0$). Solutions containing 200 g. of disodium hydrogen phosphate dodecahydrate and 3·4 g. of zinc chloride in 100 c.c. or 5 g. of cadmium chloride in 50 c.c. were mixed and placed in 500-c.c. stoppered bottles. These were completely filled and were heated in water-baths for 2 and 6 days respectively. Both compounds form small, six-sided plates, which appear to belong to the hexagonal system and are quite unlike the more or less rectangular plates of the monohydrates of the ammonium and the potassium series (Found, for zinc salt: ZnO, 44·30; Na_2O, 16·68; P_2O_5, 38·91; loss on ignition, 0·70. Calc. for $NaZnPO_4$: ZnO, 44·38; Na_2O, 16·90; P_2O_5, 38·72%. Found, for cadmium salt: CdO, 55·12; Na_2O, 13·62; P_2O_5, 30·93; loss on ignition, 0·35. Calc. for $NaCdPO_4$: CdO, 55·73; Na_2O, 13·46; P_2O_5, 30·85%). It is interesting to compare the results of the above cadmium experiment with that in Expt. C, where the heating was only maintained for a few hours.

Expt. B (*Theory, p.* 877). *Compounds of the Type* $Na_3MH(PO_4)_2$.—*Magnesium.* This was prepared by two somewhat different procedures. It formed square prisms and was quite homogeneous, and its individuality cannot be doubted. (*a*) Solutions containing 6 g. of the hydrated chloride and 200 g. of crystallised disodium hydrogen phosphate were mixed and diluted to fill a 300-c.c. stoppered bottle, then heated in a water-bath for one day. (*b*) As in (*a*), but with 400 g. of sodium phosphate in a total volume of 450 c.c. with 9 days' heating [Found: MgO, (*a*) 14·27, (*b*) 14·15; Na_2O, (*a*) —, (*b*) 32·53; P_2O_5, (*a*) 49·88, (*b*) 49·81; loss on ignition, (*a*) 4·13, (*b*) 4·18. $Na_3MgH(PO_4)_2$ requires MgO, 14·21; Na_2O, 32·71; P_2O_5, 49·93; loss, 3·16%]. The high loss on ignition was clearly due to volatilisation of sodium oxide. The *compound* can be formulated as $NaMgPO_4,Na_2HPO_4$ and is closely related to the solid solutions described in the next experiment.

Expt. C (*Theory, p.* 877). *Solid Solutions of the Type* $xNaMPO_4,Na_2HPO_4$.—By the same methods that were used in preparing the foregoing compound, manganese, copper, and cadmium yielded crystalline preparations which appeared to be perfectly homogeneous, but could not be represented by any simple formula.

Manganese. (*a*) As in (*a*) above, from 6 g. of hydrated chloride to which 10 g. of hydroxylamine hydrochloride were added to prevent oxidation, and with a total solution volume of 400 c.c. (*b*) As in (*b*) above, but with 6 g. of manganese chloride, 12 g. of hydroxylamine hydrochloride, and only 7 days' heating. (*c*) As in (*b*), but nearly a month's heating.

Analysis.	MnO, %.	Na_2O, %.	P_2O_5, %.	Loss on ignition, %.
(*a*) Found	23·86	28·46 *	44·83	3·22
Calc. for $1·15NaMnPO_4,Na_2HPO_4$	23·96	28·64	44·79	2·64
(*b*) Found	23·32	29·10 †	44·87	3·19
(*c*) Found	23·37	28·74 †	45·11	3·22
Calc. for $1·075NaMnPO_4,Na_2HPO_4$	23·27	29·07	44·94	2·74
$NaMnPO_4,Na_2HPO_4$ requires	22·54	29·53	45·08	2·86

* Weighed as Na_2SO_4 after separation of manganese and of P_2O_5 by tin and nitric acid.

† By zinc uranyl acetate method.

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* By tin and nitric acid method; weighed as sulphate.

† By zinc uranyl acetate method.

Copper. (*a*) 6 G. of the hydrated chloride in 50 c.c. of water and 400 g. of sodium phosphate were mixed (volume 450 c.c.) and heated for 12 hours in a water-bath. (*b*) As in (*a*), but with 200 g. of sodium phosphate and 11 days' heating [Found : CuO, (*a*) 33·60, (*b*) 33·58; Na_2O, (*a*) —, (*b*) 23·79; P_2O_5, (*a*) 41·67, (*b*) 41·73; loss on ignition, (*a*) 1·81, (*b*) 1·62. Calc. for $2{\cdot}5NaCuPO_4,Na_2HPO_4$: CuO, 33·37; Na_2O, 23·41; P_2O_5, 41·70; loss, 1·51%].

Cadmium. (*a*) Solutions of 5 g. of cadmium chloride in 50 c.c. of water and 200 g. of sodium phosphate were mixed and the mixture (500 c.c.) heated for one hour in the water-bath. (*b*) As in (*a*), but the volume was 400 c.c. and heating was continued for 3 hours.

Analysis.	CdO, %.	Na_2O, %.	P_2O_5, %.	Loss on ignition, %.
Found (*a*)	49·72	16·47	32·58	1·71
Calc. for $5NaCdPO_4,Na_2HPO_4$............	49·60	16·77	32·92	0·71
Found (*b*)......................................	51·47	15·70	32·67	0·72
Calc. for $7NaCdPO_4,Na_2HPO_4$	51·22	15·90	32·37	0·51

Expt. A showed that after long heating in favourable circumstances the end product of this series of solid solutions is $NaCdPO_4$.

Expt. D (*Theory, p.* 877). *The Compound* $2Na_2HPO_4,Co_3(PO_4)_2,8H_2O$.—Solutions of 6 g. of cobalt chloride hexahydrate and 200 g. of sodium phosphate were mixed and the solution (400 c.c.) heated in a stoppered bottle in a water-bath for a month. A small amount of silica and unchanged amorphous matter was easily removed from the dense, dark blue, nearly square prisms [Found : CoO, 28·75; Na_2O, 15·84; P_2O_5, 36·18; loss on ignition, 20·32. $2Na_2HPO_4,Co_3(PO_4)_2,8H_2O$ requires CoO, 28·30; Na_2O, 15·60; P_2O_5, 35·72; loss, 20·38%].

Expt. E (*Theory, p.* 878). *Solid Solutions containing Cadmium and Potassium Phosphates.*—(*a*) Solutions of 3 g. of cadmium chloride in 50 c.c. of water and 40 g. of dipotassium hydrogen phosphate were mixed and the mixture (200 c.c.) kept at room temperature for 48 hours; the original amorphous precipitate had then become converted into large leafy crystals, which in no way gave the impression of being a mixture. (*b*) As in (*a*), but the mixture was kept at room temperature for 15 days. (*c*) 3 G. of cadmium chloride and 300 g. of potassium phosphate in a volume of 750 c.c. were kept at room temperature for 3 months.

Analyses.	CdO, %.	K_2O, %.	P_2O_5, %.	Loss on ignition, %.
Found (*a*)	46·02	{ 12·57 * 12·84 † }	28·22	14·36
Calc. for (0·315A+0·685B)	45·96	12·70	28·01	13·35
Found (*b*)......................................	45·50	13·48 †	28·58	14·32
Calc. for (0·29A+0·71B)	45·57	13·23	28·15	13·06
Found (*c*)......................................	47·27	12·03 †	28·32	13·93
Calc. for (0·37A+0·63B)	46·81	11·55	27·68	13·97
Calc. for mixture considered below ...	47·40	11·89	28·04	12·89

$$\mathrm{A} = 3[\mathrm{Cd(H_2O)_4}]^{\cdot\cdot}\left[\mathrm{PO_4\ Cd\ PO_4}\ \substack{\mathrm{H}\\ \mathrm{H}}\ \mathrm{PO_4\ Cd\ PO_4}\right]^{\mathrm{VI}};$$

$$\mathrm{B} = \mathrm{K}^{\cdot}{}_4[\mathrm{Cd(H_2O)_4}]^{\cdot\cdot}\left[\mathrm{PO_4\ Cd\ PO_4}\ \substack{\mathrm{H}\\ \mathrm{H}}\ \mathrm{PO_4\ Cd\ PO_4}\right]^{\mathrm{VI}}.$$

* P_2O_5 removed by ferric chloride method, which we found was liable to give low results for the potassium.

† P_2O_5 removed by means of tin and nitric acid.

The percentage compositions calculated for the mixtures shown above agree very well with those found by analysis for (*a*) and (*b*), but with (*c*) there is a serious difference. This can be accounted for if one supposes that, during the 3 months' standing involved in the preparation, one-sixth of the solid solution has lost water to form a less hydrated one containing one cadmium ion in place of a $[Cd\ (H_2O)_4]^{\cdot\cdot}$ ion. The composition required for such a mixture is shown above.

Expt. F (*Theory, p.* 879).—The *compound* $2MnHPO_4,Mn_3(PO_4)_2,4H_2O$ was obtained as large rhombs, coloured faintly brown owing to very slight oxidation, by the pyridine method. 6 G. of crystallised manganese chloride and 4 g. of hydroxylamine hydrochloride in 580 c.c. were mixed with 420 c.c. of the pyridine–phosphoric acid solution (see Part I, Expt. M). The mixture was contained in a loosely stoppered bottle and after 3 hours' heating in the water-bath crystallisation of the precipitate was complete [Found : MnO, 48·30; P_2O_5, 39·26; H_2O, 12·96. $Mn_5H_2(PO_4)_4,4H_2O$ requires MnO, 48·70; P_2O_5, 38·96; H_2O, 12·34%].

$2CdHPO_4,Cd_3(PO_4)_2,4H_2O$. This compound was prepared in a similar way by mixing 4·5 g.

of the metal chloride in 490 c.c. of water with 210 c.c. of the pyridine–phosphoric acid solution : 3 hours' heating on the water-bath sufficed to convert the precipitate into large, thick, square-ended prisms. The analyses relate respectively to the compound prepared as above and as in Part I, Expt. M (Found : CdO, 63·43, 63·89; P_2O_5, 28·30, —; H_2O, 9·07, 8·89. Calc. : CdO, 63·20; P_2O_5, 27·96; H_2O, 8·86%).

SUMMARY.

(1) Several well-defined double orthophosphates of sodium and bivalent metals have been prepared, some being new.

(2) Several series of solid solutions have also been obtained.

(3) These appear to be closely related, although at first sight very different.

(4) Their nature has been considered.

(5) The orthophosphates, $2MHPO_4,M_3(PO_4)_2,4H_2O$, which do not contain alkali appear to have similar structures to the compounds which form the solid solutions.

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