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A Study of Inorganic Ion-exchangers. VIII.[1] The Synthesis of the Crystalline $Zr(RNH)_xH_{2-x}(PO_4)_2 \cdot yH_2O$ and Their Characteristics ($R=(C_nH_{2n+1})_3$ and C_5H_5, $n=1—6$)

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The synthesis of microcrystalline compounds with the formula of $Zr(RNH)_xH_{2-x}(PO_4)_2 \cdot yH_2O$ ($R=(C_nH_{2n+1})_3$, C_5H_5, $n=1—6$, $x=0.1—0.6$, $y=1—3$) and their characteristics have been investigated. The compounds were formed by means of a hydrothermal reaction between $RNH \cdot H_2PO_4$ and $ZrOCl_2$ in the mole ratio of 4:1 at 130—180 °C. The layer-spacings of the trimethyl-, triethyl-, tripropyl-, tributyl-, tripentyl-, trihexylamine, and pyridine phosphates were 9.9, 13.0, 13.6, 17.0, 16.5, 18.4, and 10.9 Å respectively. In the thermal decomposition of each phosphate, the water of crystallization was eliminated at 105—130 °C. The organic base group in the alkylamine phosphates was burned in the presence of air at 330—360 °C, but this combustion was imperfect in the case of pyridine phosphate. The phosphates condensed at 400—450 °C. $Zr(RNH)_xH_{2-x}(PO_4)_2 \cdot yH_2O$ was also obtained by means of an ion-exchange reaction between γ-$Zr(HPO_4)_2 \cdot 2H_2O$ and the corresponding tertiary amine. In these products, the layer-spacings of the trimethyl-, triethyl-, tripropyl-, tributyl-, tripentyl-, and trihexylamine phosphates were 17.6, 16.4, 16.7, 21.0, 21.5, and 23.2 Å respectively, while those of pyridine and piperidine phosphates were 12.4 and 18.4 Å respectively. The layer-spacings of the products increased roughly with the size of the guest molecules. When $Zr(RNH)_xH_{2-x}(PO_4)_2 \cdot yH_2O$ was treated with HCl, the products from the hydrothermal reaction changed to α-$Zr(HPO_4)_2 \cdot H_2O$, while the products from the ion-exchange reaction returned to γ-$Zr(HPO_4)_2 \cdot 2H_2O$ the raw material.

Recently, inorganic layer structure compounds have been considered to be materials with specific functions. Titanium and zirconium phosphates are useful compounds for ion-exchange, though a compound with a large layer-spacing can not be obtained as a result of the use of hydrogen and exchanged metal ions which are small in radius. The large layer-spacing compounds performing a chemical embellishment are promising as materials with specific functions as catalysers. Zirconium phosphates containing an organic radical have been obtained by means of ion-exchange reactions between α-,β-zirconium(IV) bis(hydrogenorthophosphate) and pyridine,[2] or butylamine.[3] The organo-derivatives of zirconium phosphate with a P–O–P ester bond were obtained by the reactions of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ with ethylene oxide[4] or propylene oxide.[5] By another method, microcrystalline compounds with the $Zr(HOCH_2PO_3)_2 \cdot H_2O$, $Zr(C_6H_5PO_3)_2$, and $Zr(C_2H_5OPO_3)_2$ formulae were formed by slowly decomposing the fluorozirconium complex in the presence of $HOCH_2PO(OH)_2$, $C_6H_5PO(OH)_2$, and $PO(OC_2H_5)_2$.[6]

To develop an inorganic ion-exchanger, we synthesized γ-zirconium phosphate by means of a hydrothermal reaction between $ZrOCl_2$ and MH_2PO_4 (M=Na, K, NH_4).[1] For the present studies, $RNH \cdot H_2PO_4$ ($R=(C_nH_{2n+1})_3$, C_5H_5, $n=1—6$) was prepared by the reaction of phosphoric acid with tertiary amine, while $Zr(RNH)_xH_{2-x}(PO_4)_2$, with a larger layer-spacing than γ-$Zr(HPO_4)_2 \cdot H_2O$, was formed by a hydrothermal reaction between $RNH \cdot H_2PO_4$ and $ZrOCl_2$ in an autoclave. The synthesis conditions were determined, and the characteristics of the product were investigated and compared with those of a product obtained by the ion-exchange between γ-$Zr(HPO_4)_2 \cdot 2H_2O$ and the corresponding tertiary amine.

Experimental

Direct Method Synthesizing $Zr(RNH)_xH_{2-x}(PO_4)_2$. By refluxing between 1 mol of reagent-grade tertiary amine, 1 mol of 85% phosphoric acid, and a little water, an oily tertiary amine phosphate, $RNH \cdot H_2PO_4$ ($R=(C_nH_{2n+1})_3$, C_5H_5, $n=1—6$), was prepared beforehand for the following purpose.

In a 20 cm³-hard glass tube, 1.61 g of $ZrOCl_2 \cdot 8H_2O$, 2—12 g of $RNH \cdot H_2PO_4$, and 5 cm³ of water were taken. The contents were then thoroughly mixed, and the tube was sealed. 1—4 sealed tubes thus prepared under varying conditions were placed in a 200-cm³ stainless steel autoclave with 80 cm³ of water to prevent the rupture of the glass tubes. The autoclave was then heated at 120—180 °C. The products in the tube were separated from the mother liquors, washed with water, and then dried at 20 °C in a relative humidity (R.H.) of 75%. In direct synthesis by means of a 300-cm³ autoclave lined with Hastelloy-B, 5—20 times as much of the raw materials were used, and the products were obtained with the above methods.

Formation of $Zr(RNH)_xH_{2-x}(PO_4)_2$ by Means of the Ion-exchange Method. In a 200-cm³ Erlenmeyer flask, one gram of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ 0.91—8.07 g of tertiary amine and 100 dm³ of water were mixed and stirred for 24 h at 50 °C; the product thus obtained was separated, washed by means of a centrifugal separator, and finally dried.

Analysis. The P_2O_5 and ZrO_2 as components of the reaction product were determined according to the previously reported methods.[1] H_2O was obtained by deducting the weight of the Tertiary amine from the weight loss of the sample heated at 800 °C. Tertiary amine was obtained by the ammonia-distillation method.

The X-ray diffraction was performed with a Shimadzu Seisakusho diffractometer, using Ni filtered Cu $K\alpha$ radiation at 30 KVP and 20 mA. A Rigaku Denki micro-thermal analyzer with 100 μV of DTA sensibility and 20 mg of TG sensibility was used for the thermal analysis.

Results and Discussion

Reactions of $ZrOCl_2$ with $RNH \cdot H_2PO_4$ (Direct-synthesizing Method). The conditions for the synthesis of $Zr(RNH)_xH_{2-x}(PO_4)_2$ and the analytical data of the products are shown in Table 1.

The influence of the $RNH \cdot H_2PO_4$/Zr mole ratios on the hydrothermal reaction between $(C_2H_5)_3NH \cdot H_2PO_4$

Table 1. Synthesis of $Zr(RNH)_xH_{2-x}(PO_4)_2$ and their analysis ($R=(C_nH_{2n+1})$, C_5H_5, $n=1—6$)

	Reaction conditions								Reaction products					
No.	$ZrOCl_2 \cdot 8H_2O$ (g)	$RNH \cdot H_2PO_4$ Tertiary amine	(%)	(g)	H_2O (ml)	$RNH \cdot H_2PO_4$/Zr (mole ratio)	Temp °C	Time h	Mother liquor (pH)	ZrO_2 (%)	P_2O_5 (%)	Tertiary amine (%)	H_2O (%)	ZrO_2 : P_2O_5 : Tertiary amine : H_2O (mole ratio)
1	1.61	$(C_2H_5)_3N$	83.6	2.38	5	2.0	150	120	1.96	35.5	40.8	3.45	20.4	1.0 : 1.0 : 0.12 : 4.0
2	1.61	$(C_2H_5)_3N$	83.6	3.57	5	3.0	150	120	2.13	34.9	40.2	11.7	13.2	1.0 : 1.0 : 0.41 : 2.6
3	1.61	$(C_2H_5)_3N$	83.6	4.76	5	4.0	150	120	2.23	33.5	38.5	14.8	12.0	1.0 : 1.0 : 0.58 : 2.5
4	3.88	$(C_2H_5)_3N$	99.0	12.3	5	5.14	150	120	2.41	33.2	38.3	15.7	12.3	1.0 : 1.0 : 0.57 : 2.5
5	1.61	$(C_2H_5)_3N$	99.0	9.52	5	8.0	150	120	2.74	33.1	38.1	16.5	12.3	1.0 : 1.0 : 0.60 : 2.5
6	1.61	$(C_2H_5)_3N$	83.6	4.76	5	4.0	130	120	2.26	33.2	38.3	16.6	12.0	1.0 : 1.0 : 0.60 : 2.5
7	1.61	$(n\text{-}C_3H_7)_3N$	99.0	4.75	5	4.0	130	120	2.04	35.5	40.9	7.36	16.3	1.0 : 1.0 : 0.18 : 3.1
8	1.61	$(n\text{-}C_4H_9)_3N$	99.0	5.67	5	4.0	130	120	1.95	31.4	35.5	19.0	14.3	1.0 : 1.0 : 0.40 : 3.1
9	1.61	C_5H_5N	91.3	3.89	5	4.0	130	120	2.42	34.7	40.1	4.46	21.1	1.0 : 1.0 : 0.20 : 4.1
10	1.61	$(C_2H_5)_3N$	83.6	4.76	5	4.0	160	96	2.42	33.8	39.0	14.9	12.3	1.0 : 1.0 : 0.54 : 2.5
11	1.61	$(n\text{-}C_3H_7)_3N$	99.0	4.75	5	4.0	160	96	2.12	36.2	41.8	5.81	16.1	1.0 : 1.0 : 0.14 : 3.0
12	1.61	$(n\text{-}C_4H_9)_3N$	99.0	5.67	5	4.0	160	96	2.51	34.6	39.8	12.9	12.7	1.0 : 1.0 : 0.25 : 2.5
13	1.61	C_5H_5N	91.0	3.89	5	4.0	160	96	2.23	34.9	40.2	5.13	19.8	1.0 : 1.0 : 0.23 : 3.9
14	1.61	$(C_2H_5)_3N$	83.6	4.76	5	4.0	180	96	2.38	32.9	37.8	15.4	13.9	1.0 : 1.0 : 0.58 : 2.9
15	1.61	$(n\text{-}C_3H_5)_3N$	99.0	4.75	5	4.0	180	96	2.25	37.9	43.6	3.98	14.5	1.0 : 1.0 : 0.091 2.6
16	1.61	$(n\text{-}C_4H_9)_3N$	99.0	5.67	5	4.0	180	96	2.26	33.6	38.7	15.0	12.7	1.0 : 1.0 : 0.29 : 2.6
17	1.61	C_5H_5N	91.0	3.89	5	4.0	180	96	2.31	34.9	40.2	5.52	19.2	1.0 : 1.0 : 0.25 : 3.7
18	16.1	$(CH_3)_3N$	57.0	55.1	10	4.0	150	24	2.60	36.9	42.5	9.2	11.4	1.0 : 1.0 : 0.51 : 2.1
19	16.1	$(C_2H_5)_3N$	83.6	47.6	45	4.0	140	24	2.65	35.6	41.1	15.2	8.1	1.0 : 1.0 : 0.51 : 1.5
20	32.2	$(n\text{-}C_3H_7)_3N$	86.7	109.8	40	4.0	140	24	2.14	35.8	41.2	9.0	14.0	1.0 : 1.0 : 0.21 : 2.6
21	16.1	$(n\text{-}C_4H_9)_3N$	80.0	70.9	40	4.0	140	24	2.67	32.1	36.9	23.0	8.0	1.0 : 1.0 : 0.47 : 1.7
22	8.05	$(n\text{-}C_5H_{11})_3N$	60.0	54.2	21	4.0	150	24	2.32	36.6	45.9	8.1	7.0	1.0 : 1.0 : 0.10 : 1.2
23	8.05	$(n\text{-}C_6H_{13})_3N$	90.2	39.9	30	4.0	150	24	2.10	33.6	29.2	32.8	4.4	1.0 : 1.0 : 0.51 : 1.0
24	32.2	C_5H_5N	91.3	77.8	50	4.0	140	24	3.01	39.9	45.9	5.0	9.2	1.0 : 1.0 : 0.20 : 1.6

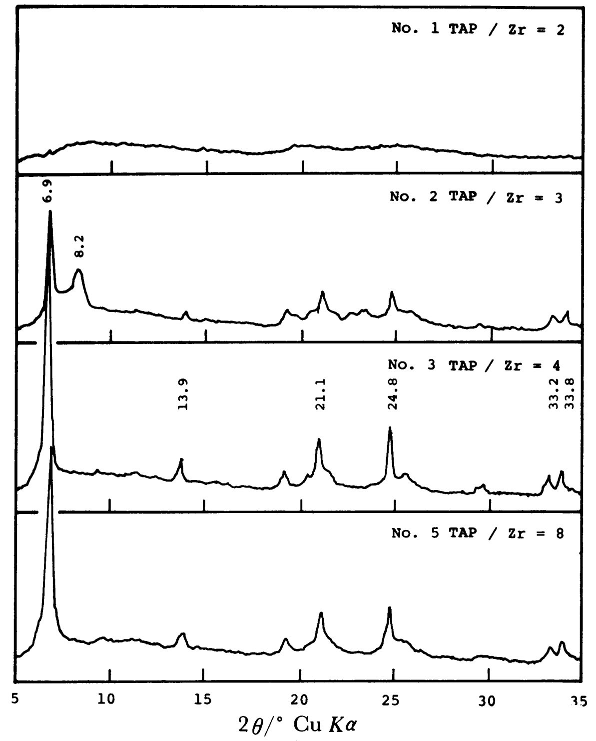


Fig. 1. X-Ray diffraction patterns of $Zr[(C_2H_5)_3NH]_xH_{2-x}(PO_4)_2$. (Influence of mole ratios of $(C_2H_5)_3NH \cdot H_2PO_4/ZrOCl_2$).
Numerals on the peaks indicate 2θ/°

and $ZrOCl_2$ were examined in Nos. 1—5 of Table 1; the X-ray diffraction patterns of the reaction products are shown in Fig. 1.

In the $RNH \cdot H_2PO_4/Zr$ mole ratio of 2 (No. 1), an amorphous product was formed, though in the X-ray diffraction pattern of the product in the $RNH \cdot H_2PO_4/Zr$ mole ratio of 3, the peaks appeared at 6.9 and 8.2°. In the products of the $RNH \cdot H_2PO_4/Zr$ mole ratios of 4 (No. 3) and 8 (No. 5), the peak intensity of 6.9° increased and the peak of 8.2° disappeared completely. In Nos. 3, 4, and 5, crystalline products with roughly regular components were obtained. It is considered, therefore, that $RNH \cdot H_2PO_4/Zr$ mole ratios of 4 or more are suitable for the synthesis of $Zr(RNH)_xH_{2-x}(PO_4)_2$, which can be written as follows;

$$ZrOCl_2 + 2RNH\,H_2PO_4 \longrightarrow Zr(RNH)_xH_{2-x}(PO_4)_2 + 2\text{-}x\,RNHCl + xHCl + H_2O.$$

In the hydrothermal synthesis of γ-$ZrNH_4H(PO_4)_2$,[1] the pH values of the reaction solution were in the range of 2.15—3.56; we are also shown as 2—3 in the formation of $Zr(RNH)_xH_{2-x}(PO_4)_2$.

Influence of Reaction Temperatures: An amorphous product was formed in the mother liquor at temperatures lower than 100 °C. The product crystallized above 120 °C, and the crystallinity was augmented with the elevation of the reaction temperature. The product was red-browned by the thermal decomposition of tertiary amine at 180 °C or higher. In an X-ray diffraction pattern of the reaction product at 250 °C, the diffraction peak-characterized product decreased in intensity; however, the X-ray diffraction peaks of the α-$Zr(HPO_4)_2 \cdot H_2O$ formed as a result of the decomposition of the product appeared anew. It may be concluded, therefore, that heating at 130—180 °C is suitable for the synthesis of $Zr(RNH)_xH_{2-x}(PO_4)_2$.

Composition of Reaction Products: Examples of various reaction conditions are shown in Nos. 6—24 of Table 1.

From the analytical data, the chemical formulae of the products dried in R.H. 75% can be written as follows: $Zr[(CH_3)_3NH]_{0.5}H_{1.5}(PO_4)_2 \cdot 2H_2O$, $Zr[(C_2H_5)_3NH]_{0.5}H_{1.5}(PO_4)_2 \cdot 1.5—2.0H_2O$ (No. 19 Product dried in R.H. 0%; 0.5 hydrate), $Zr[(C_3H_7)_3NH]_{0.1-0.2}H_{1.9-1.8}(PO_4)_2 \cdot 1.5—2.0H_2O$, (No. 20 Product dried in R.H.

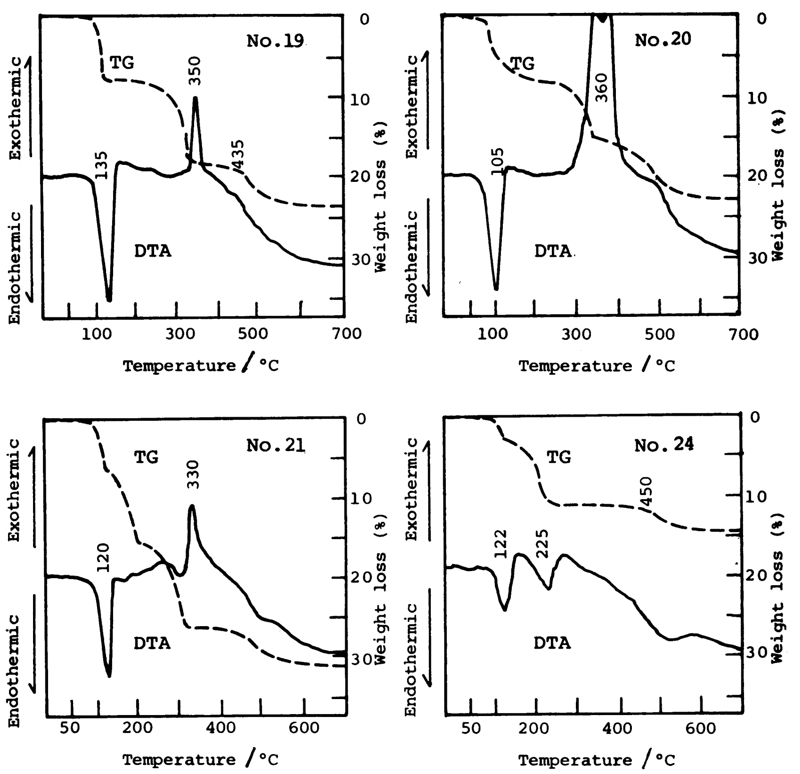


Fig. 2. DTA and TG curves of $ZrRNH_xH_{2-x}(PO_4)_2$ (R= $(C_2H_5)_3$, $(C_3H_7)_3$, $(C_4H_9)_3$, C_5H_5).
No. 19: $Zr[(C_2H_5)_3NH]_{0.5}H_{1.5}(PO_4)_2\cdot 0.5H_2O$, No. 20: $Zr[(C_3H_7)_3\cdot NH]_{0.2}H_{1.8}(PO_4)_2\cdot 1.6H_2O$, No. 21: $Zr[(C_4H_9)_3NH]_{0.5}H_{1.5}(PO_4)_2\cdot 0.7H_2O$, No. 24: $Zr(C_5H_5NH)_{0.2}H_{1.8}(PO_4)_2\cdot 0.6H_2O$

TABLE 2. FORMATION AND ANALYSIS OF REACTION PRODUCTS BETWEEN γ-$Zr(HPO_4)_2\cdot 2H_2O$ AND TERTIARY AMINE

	Reaction conditions								Reaction products					
No.	γ-$Zr(HPO_4)_2$ $\cdot 2H_2O$ (g)	Tertiary amine Compound	(g)	H_2O (C_2H_5OH) (ml)	Tertiary amine / Zr (mole ratio)	Temp °C	Time h	Dry (temp/°C R.H/%)	ZrO_2 (%)	P_2O_5 (%)	Tertiary amine (%)	H_2O (%)	ZrO_2 : P_2O_5 : Tertiary amine : H_2O (mole ratio)
1	1.00	$(CH_3)_3N$	1.86 (57%)	100	3.0	25	30	20, 75	34.6	39.8	12.8	12.9	1.0 : 1.0 : 0.77 : 2.56
2	1.00	$(C_2H_5)_3N$	0.91	100	3.0	50	24	20, 75	39.1	33.9	16.5	10.5	1.0 : 1.0 : 0.59 : 2.12
3	1.00	$(n\text{-}C_3H_7)_3N$	4.29	100	9.5	50	24	20, 0	41.1	35.6	13.1	10.3	1.0 : 1.0 : 0.31 : 1.98
4	1.00	$(n\text{-}C_4H_9)_3N$	5.59	100	9.5	50	24	20, 75	35.2	30.6	21.0	13.2	1.0 : 1.0 : 0.45 : 2.95
5	1.00	$(n\text{-}C_5H_{11})_3N$	6.82	5 (95)	9.5	25	30	20, 0	32.4	37.3	30.8	0.0	1.0 : 1.0 : 0.52 : 0.0
6	1.00	$(n\text{-}C_6H_{13})_3N$	8.07	5 (95)	9.5	25	30	20, 0	30.1	34.7	32.8	2.4	1.0 : 1.0 : 0.49 : 0.56
7	1.00	C_5H_5N	2.22	100	9.5	45	24	20, 75	44.7	38.8	8.39	8.0	1.0 : 1.0 : 0.54 : 3.18
8	1.00	$C_5H_{11}N$	2.55	100	9.5	25	30	20, 75	32.8	37.7	16.4	13.1	1.0 : 1.0 : 0.72 : 2.73

0%; 0.7 hydrate), $Zr[(C_4H_9)_3NH]_{0.3-0.5}\cdot H_{1.7-1.5}(PO_4)_2\cdot 1.5$—$2.0H_2O$ (No. 21 Product dried R.H. 0%; 0.7 hydrate). $Zr(C_5H_5NH)_{0.2-0.25}H_{1.8-1.75}(PO_4)_2\cdot 2.5$—$3.0H_2O$ (No. 24 Product dried R.H. 0%; 0.6 hydrate). The mole ratios of tertiary amine/P_2O_5 in the product showed the following order: methylamine=ethylamine > butylamine > pyridine > propylamine phosphates. It is considered that the order is influence by the basicity, size, and structure of the tertiary amines.

Behavior of Thermal Decomposition: The DTA and TG curves of $Zr(RNH)_xH_{2-x}(PO_4)_2\cdot yH_2O$ are shown in Fig. 2.

The products released the water of crystallization at 105—135 °C, and an endothermic peak appeared on the TG curve. In the trialkylamine phosphates of Nos. 19—21, an exothermic peak owing to the combustion of the amine radical appeared at 330—360 °C, but the exothermic peak could not be recognized because of the incomplete combustion of the aromatic radical in the pyridine phosphate of No. 24.

The formation of pyrophosphate attributable to the condensation of orthophosphate occured at 400—450 °C. This temperature was higher than that of γ-$Zr(HPO_4)_2\cdot 2H_2O$. Therefore, the $Zr(RNH)_xH_{2-x}(PO_4)_2$, which preserved its layer structure until 400 °C, can be considered to be a catalytic functional material.

Ion-exchange between γ-$Zr(HPO_4)_2\cdot 2H_2O$ *and Tertiary Amines.* The conditions for the formation of $Zr(RNH)_xH_{2-x}(PO_4)_2$ and the analytical data of the products are shown in Table 2.

We are afraid that, as $(CH_3)_3N$ and $(C_2H_5)_3N$ have a stronger basicity than the other tertiary amines, γ-

$Zr(HPO_4)_2 \cdot 2H_2O$ as a acid salt was dissolved in the solution of the excess amine. Consequently, the amounts of $(CH_3)_3N$ and $(C_2H_5)_3N$ used were 1/3 equivalents as compared with those of the other tertiary amines. The P_2O_5 contents were about the same as those in the corresponding products obtained by the direct synthesizing method, while the tertiary-amine contents in the trimethylamine, tripropylamine, and pyridine phosphates were larger than in the products of the direct-synthesizing method. The tertiary-amine contents in the tripropylamine phosphates obtained by both methods were less than in the other phosphates. All the products dried in 75 % R.H. at 20 °C have 1—2 mol of the water of crystallization. It can be expected that one molecular layer of water is held between the upper and lower phosphate layers.

Layer-spacing and Orientation of Tertiary Amines. The layer-spacing was determined from a first d value (002) of the X-ray diffraction pattern. The layer-spacings of the trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, trihexylamine, and pyridine phosphates obtained by the direct-synthesizing method were 9.9, 13.0, 13.6, 17.0, 16.5, 18.4, and 10.9 Å, (Å$=10^{-10}$ m) respectively. On the other hand, the layer-spacings of trimethylamine, triethylamine, tripropylamine, tributylamine, pyridine, and piperidine phosphates were 17.66, 16.4, 16.7, 21.0, 21.5, 23.2 12.4, and 18.4 Å respectively.

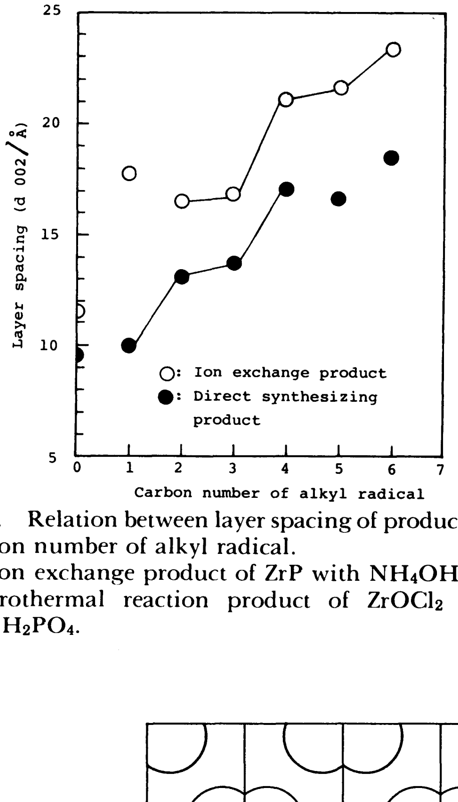


Fig. 3. Relation between layer spacing of product and carbon number of alkyl radical.
○: Ion exchange product of ZrP with NH_4OH. ●: Hydrothermal reaction product of $ZrOCl_2$ with $NH_4H_2PO_4$.

The relation between the layer-spacing of the product and the carbon number of the alkyl group is plotted in Fig 3. In this diagram, the two points at carbon number=0 indicate the layer-spacing of the ion-exchange product between γ-$Zr(HPO_4)_2 \cdot 2H_2O$ with aqueous ammonia and that of the hydrothermal reaction product of $ZrOCl_2$ with $NH_4H_2PO_4$ respectively. The layer-spacing increased with an increase in the carbon numbers of the alkyl group, with the exceptions of the trimethylamine phosphate produced by the ion-exchange and the tripentylamine phosphate produced by the direct method. However, the values of layer-spacing in the cases of n=odd number approximated to that in the cases of $n-1$. The upper and the lower phosphate layers were each connected with the tertiary amines which were sandwiched in the layers. Moreover the C_nH_{2n+1} molecules are considered to be oriented in a step-by-step manner, as is in Fig. 4.

The analytical data in Table 1 show tertiary amine/ZrO_2=0.5 in the products of $n \leqslant 2$ and tertiary amine/ZrO_2=0.1—0.5 in the products of $n \geqslant 3$. If the

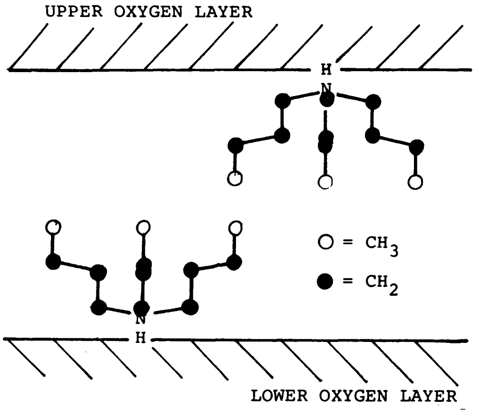
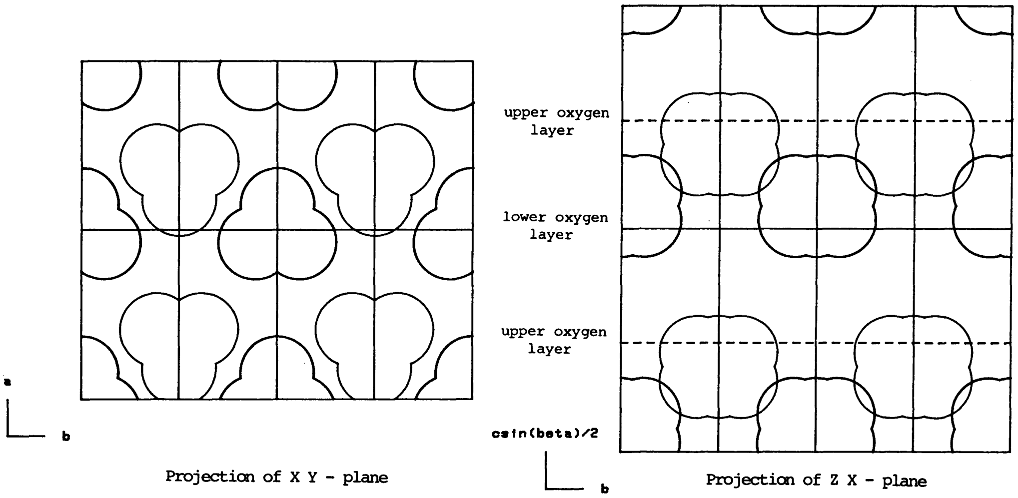


Fig. 4. Interlayer model of $Zr(C_3H_7)_3NH_xH_{2-x}(PO_4)_2$.



Projection of X Y - plane

Projection of Z X - plane

Fig. 5. Configuration of $(C_2H_5)_3N$ in layer spacing of α-$Zr(HPO_4)_2 \cdot H_2O$.

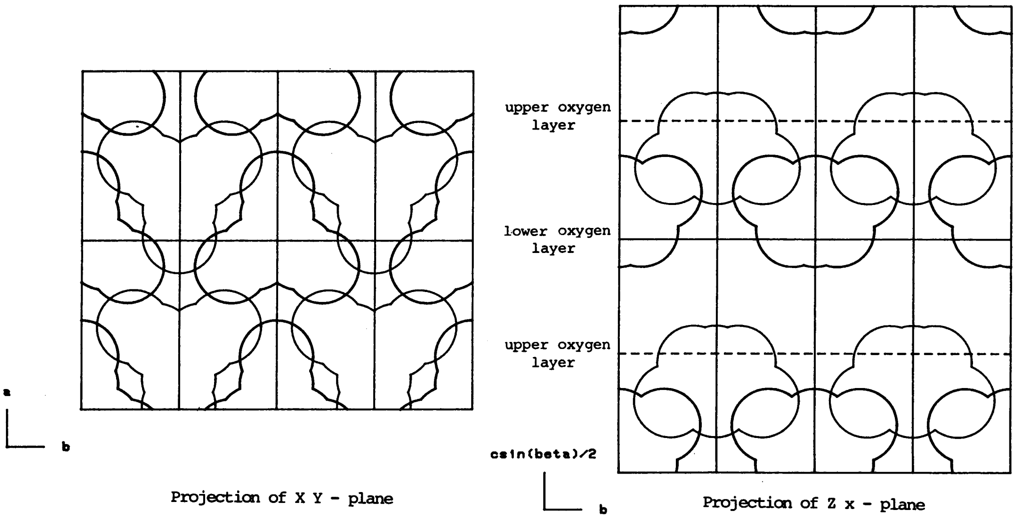


Fig 6. Configuration of $(C_3H_7)_3N$ in layer spacing of α-$Zr(HPO_4)_2$.

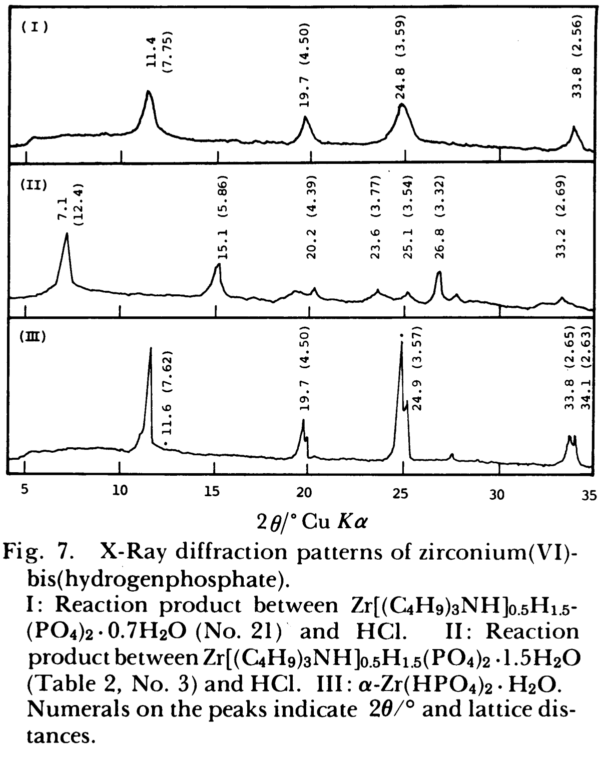


Fig. 7. X-Ray diffraction patterns of zirconium(VI)-bis(hydrogenphosphate).
I: Reaction product between $Zr[(C_4H_9)_3NH]_{0.5}H_{1.5}(PO_4)_2 \cdot 0.7H_2O$ (No. 21) and HCl. II: Reaction product between $Zr[(C_4H_9)_3NH]_{0.5}H_{1.5}(PO_4)_2 \cdot 1.5H_2O$ (Table 2, No. 3) and HCl. III: α-$Zr(HPO_4)_2 \cdot H_2O$. Numerals on the peaks indicate 2θ/° and lattice distances.

value of tertiary amine/ZrO_2 is 0.5, and if the van der Waals radii of CH_2 and CH_3 in the alkyl group are 2 Å, then the arrangement of alkyl groups between the layers of α-$Zr(HPO_4)_2 \cdot H_2O$ may be as projected in Fig. 5 (triethylamine phosphate) and in Fig. 6 (tripropylamine phosphate). If $n \leqslant 2$, the amine molecules between layers of α-$Zr(HPO_4)_2 \cdot H_2O$ are not adjacent to each other and are arranged in a packed state. However ,if $n \geqslant 3$, the products actually have the tertiary amine/ZrO_2 values are 0.1—0.5; consequently, the amine molecules are oriented so as to avoid contact with each other.

Acid Salts of $Zr(RNH)_xH_{2-x}(PO_4)_2$. The X-ray diffraction patterns of the acid salts which are obtained by a hydrochloric acid treatment of the direct-synthesizing and ion-exchange products, and that of α-$Zr(HPO_4)_2 \cdot H_2O$ are shown in Fig. 7.

The direct-synthesizing method is similar to the preparation of $ZrNH_4H(PO_4)_2$[1] as a raw material of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ and the layer-spacing of tributylamine phosphate obtained by the direct-synthesizing method shows a large 17 Å value. It can be simply expected, therefore, that the tributylamine phosphate has the γ-form. Howevere, the X-ray diffraction pattern (I) of the acid-treatment salt of the tributylamine phosphate agreed with that (III) of α-$Zr(HPO_4)_2 \cdot H_2O$. This fact was observed in the acid-treatment salts of the triethylamine, tripropylamine and pyridine phosphates, while the X-ray diffraction pattern (II) of the acid-treatment salt of the tributylamine phosphate obtained by the ion-exchange agreed with that of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ the raw material. A similar phenomenon was also observed in the acid-treatment salts of other $Zr(RNH)_xH_{2-x}(PO_4)_2$ (R=Et, Pr, C_5H_5).

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