

layer were recognized in all crystals. This lithium-intercalated complex is very hygroscopic. It was observed that the long reaction times yielded amorphous products.

In the present study, we obtained some different chemical analysis data which widely deviated from theoretical; that is, higher lithium content ($\text{Li}_n\text{V}(\text{CH}_3\text{CS}_3)_2$ for $1 < n \leq 3$) and less organic component were detected. This deviation of the chemical analysis data resulted from the partial dissolving of the surface organic layers of the intercalated complex during the reduction reaction by *n*-butyllithium in hexane. From X-ray diffraction of the samples which were completely dried under vacuum and kept in a desiccator, no lattice expansion in the a_0 dimension was observed. Whereas in the case of the samples which were left in air for 1 day, the basal spacing increased to 10.7 Å. From IR and thermal analysis it was found that this increase of the basal spacing was due to interlayer water adsorption in the host materials. In the IR spectrum, bands at 3380 and 1620 cm^{-1} were attributed to the vibrations of the H_2O molecule. An endothermic peak with a weight loss of 10% was found at around 100 °C. The electrical resistivities of $\text{V}(\text{CH}_3\text{CS}_3)_2$ and its lithium-intercalated complex were found to be greater than $10^6 \Omega \text{ cm}$ at room temperature.

Summary

In the present study a new type of layered compound $\text{V}(\text{CH}_3\text{CS}_3)_2$ was prepared, and it was found that the compound could form a lithium-intercalation complex by the reaction with *n*-butyllithium.

Acknowledgment. The authors wish to thank Mrs. Fukuda for C, H, and S chemical analyses.

Registry No. $\text{V}(\text{CH}_3\text{CS}_3)_2$, 76721-85-2; VOCl_2 , 10213-09-9; CH_3CSOH , 507-09-5; *n*- $\text{C}_4\text{H}_9\text{Li}$, 109-72-8.

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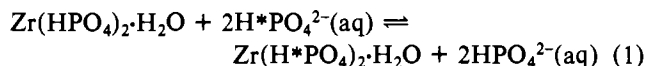
Exchange of Interlayer Hydrogen Orthophosphate Ions of Zirconium Bis(hydrogen orthophosphate) Dihydrate with Phenylphosphonate Ions

Shoji Yamanaka* and Makoto Hattori

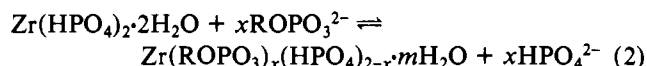
Received July 30, 1980

Zirconium bis(hydrogen orthophosphate) is an insoluble ion exchanger with layer structure. The mono- and dihydrate, $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, are known, which are called α - and γ -zirconium phosphate, respectively.¹⁻³ Water molecules reside between the layers. Both forms consist of ZrO_6 octahedra lying on a plane and $\text{PO}_3(\text{OH})$ tetrahedra. Every $\text{PO}_3(\text{OH})$ tetrahedron situated above and below the plane shares its three oxygen corners with three different ZrO_6 octahedra. In the structure of γ form, these octahedra and tetrahedra are more densely linked than those of the α form.^{3,4}

Rahman and Barrett^{5,6} investigated the exchange of phosphate ions of α -zirconium phosphate in aqueous solutions using ^{32}P isotope in a heterogeneous system. They have reported that phosphate groups of internal as well as outer surfaces of α -zirconium phosphate crystals can be exchanged with phosphate groups of the contacting solution according to eq 1, where $\text{H}^*\text{PO}_4^{2-}$ represents phosphate groups labeled with ^{32}P isotope.



In a series of previous studies,^{7,8} we have reported that the interlayer HPO_4^{2-} ions of γ -zirconium phosphate can be reversibly exchanged with various orthophosphoric ester ions of the type ROPO_3^{2-} when γ -zirconium phosphate crystals are heated with the corresponding orthophosphoric acid ester solutions above 70 °C:



where R stands for an organic group such as phenyl, allyl, ether, *n*-alkyl, aminoethyl, and chloroethyl. This exchange reaction seems to be more widely applicable not only to phosphate ester ions but also to various phosphorus compounds having the group.



The present paper is concerned with the exchange of the interlayer HPO_4^{2-} ions of γ -zirconium phosphate with phenylphosphonate ions ($\text{C}_6\text{H}_5\text{PO}_3^{2-}$) which are much more stable than phosphate ester ions against heating and hydrolysis.

Experimental Section

Exchange Procedure. The experimental procedure was similar in principle to that described for the exchange with phenyl orthophosphate ions.⁷ γ -Zirconium phosphate (about 1 g) was dispersed into 100 mL of 1 M phenylphosphonic acid solution in a mixture of equal volumes of acetone and water and heated under reflux for 20 h. When the pot temperature for the heating was below 60 °C, the reaction did not occur. The dispersed solution was renewed, and the refluxing was repeated to ensure the completion of the reaction. The solid sample was separated by using a Teflon filter, washed with acetone and dried in air.

Analyses. The exchanged product was ignited to oxide at 1000 °C. A weighed amount (about 200 mg) of the ignition product was dissolved with 1 g of molten Na_2CO_3 - K_2CO_3 mixture. The solidified melt was dissolved in 100 mL of water. Zirconium remained undissolved in the solution as an oxide. The oxide residue was separated by filtration followed by washing with 50 mL of hot 4% Na_2CO_3 solution and 50 mL of 1 M NH_3 . The zirconium content was determined gravimetrically by ignition of the residue to ZrO_2 . The filtrate together with the washings was used to determine the phosphorus content by the colorimetric method of Bernheit and Wreath.⁹

Results and Discussion

The basal spacing of γ -zirconium phosphate was enlarged from 12.27 to 15.14 Å by the refluxing. Electron microscopic examination showed that the size of the initial γ -zirconium phosphate platelets ($5 \times 0.5 \mu\text{m}^2$) was retained by the refluxing and moreover that the electron diffraction patterns obtained on the refluxed platelets with the plane perpendicular to the electron beam were very similar to that of the initial γ -zirconium phosphate shown previously.³ These results indicate

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Table I. Comparison of Crystal Lattice Parameters of $Zr(HPO_4)_2 \cdot 2H_2O$ and $Zr(C_6H_5PO_3)_{0.5}(HPO_4)_{1.5} \cdot 2H_2O$

	$Zr(HPO_4)_2 \cdot 2H_2O^a$	$Zr(C_6H_5PO_3)_{0.5}(HPO_4)_{1.5} \cdot 2H_2O$
form	monoclinic	orthorhombic
<i>a</i> , Å	5.376	5.377 (4)
<i>b</i> , Å	6.636	6.644 (6)
<i>c</i> , Å	24.56	15.14 (1)
β , deg	93.94	...
Z	4	2

^a Reference 3.

that the two-dimensional structure of γ -zirconium phosphate is unchanged during the reaction with phenylphosphonic acid although the basal spacing is increased.

The chemical properties of the exchanged products were very similar to those of the products obtained by the exchange of phosphate ions of γ -zirconium phosphate with phosphate esters.^{7,8} The product could persist in 1 M HCl at 95 °C for 1 day without any change in the basal spacing, whereas it reverted to the initial γ -zirconium phosphate by heating with 1 M orthophosphoric acid at 90 °C for several hours. The product was easily hydrolyzed into a gel in 1 M NaOH even at room temperature. The gel, zirconium hydroxide, was separated by filtration, washed with water, and converted to ZrO_2 on heating. The filtrate was analyzed by cellulose thin-layer chromatography according to the procedure described previously.¹⁰ Two spots for $C_6H_5PO_3^{2-}$ and PO_4^{3-} ions were observed in the chromatogram at $R_f = 0.68$ and 0.36, respectively.

The exchanged product was dispersed in acetone and spread on a NaCl crystal plate to measure the infrared spectrum. Sharp infrared absorption bands appearing at 1445, 758, 730, and 698 cm^{-1} were attributed to the P–C stretching vibration and the out-of-plane deformation vibrations of the monosubstituted phenyl group. Those absorption bands coincided in position with the main absorption bands of phenylphosphonic acid. Absorptions that would arise from adsorbed acetone were not observed in the spectrum of the exchanged product of γ -zirconium phosphate.

The amounts of exchanged phenylphosphonate ions and adsorbed water were determined by thermogravimetric analysis as used in previous studies.^{7,8} The composition found for the exchanged product was $Zr(C_6H_5PO_3)_{0.49}(HPO_4)_{1.51} \cdot 1.9H_2O$. This indicates that only one-fourth of the interlayer HPO_4^{2-} ions are exchangeable with $C_6H_5PO_3^{2-}$ ions. The formula for the exchanged product can be written as $Zr(C_6H_5PO_3)_{0.5}(HPO_4)_{1.5} \cdot 2H_2O$. The results in elemental analysis also support this formula. Anal. Calcd: C, 10.31; H, 2.29; ZrO_2 , 35.29; P_2O_5 , 40.65. Found: C, 9.68; H, 2.10; ZrO_2 , 35.44; P_2O_5 , 40.23. The interlayer water was reversibly desorbed by heating at 100 °C. The anhydrous form has a basal spacing of 14.4 Å. The phenyl groups of the exchanged phosphonate groups in the interlayer of γ -zirconium phosphate began to decompose above 380 °C. This temperature is much higher than the decomposition temperatures (220–260 °C) observed for the interlayer phosphate ester ions.^{7,8}

The X-ray powder pattern of the exchanged product was measured by using Ni-filtered Cu $K\alpha$ radiation. The pattern was indexed as orthorhombic. The unit-cell dimensions of the product are compared with those of the initial γ -zirconium phosphate (monoclinic) in Table I. The X-ray diffraction pattern of the product is given in Table II. As mentioned above, the *a* and *b* lattice constants of these compounds are approximately the same, indicating that the structure of the phosphate layer is maintained during the exchange. It was

Table II. X-ray Powder Diffraction Data of $Zr(C_6H_5PO_3)_{0.5}(HPO_4)_{1.5} \cdot 2H_2O$

<i>hkl</i>	<i>d</i> _{calcd} , Å	<i>d</i> _{obsd} , Å	<i>I</i>
001	15.14	15.12	vs
002	7.57	7.57	vw
011	6.08	6.08	s
101	5.06	5.06	w
012	4.99	4.98	w
102	4.38	4.38	s
111	4.03	4.03	w
112	3.66	3.67	s
020	3.32	3.31	m
021	3.24	3.24	m
104	3.10	3.10	w
005	3.03	3.03	w
121	2.778	2.776	w
200	2.689	2.688	w
201	2.647	2.650	w
006	2.524	2.523	vw
211	2.459	2.463	w
124	2.265	2.268	w
204	2.192	2.189	w
222	2.014	2.011	m

not necessary to use a supercell to index the X-ray diffraction pattern although only one-fourth of the HPO_4^{2-} ions were exchanged with $C_6H_5PO_3^{2-}$ ions. The formation of the superlattice was not observed even in the electron diffraction patterns. The unit cell contains two $Zr(HPO_4)_{1.5}(C_6H_5PO_3)_{0.5} \cdot 2H_2O$; that is, one HPO_4^{2-} ion out of four HPO_4^{2-} ions in every unit cell is exchanged with one $C_6H_5PO_3^{2-}$ ion. It is apparent that the superlattice is not formed in this crystal whether the exchanged $C_6H_5PO_3^{2-}$ ions are ordered or not.

A similar type of compound was prepared by precipitation from hydrofluoric acid solution of zirconium and phenylphosphonic acid.¹¹ The precipitate has a composition $Zr(C_6H_5PO_3)_2$, and its X-ray diffraction pattern is different from that given in Table II. The precipitate is considered to have a structure of α -zirconium phosphate type, where ZrO_6 and $PO_3(OH)$ polyhedra are more loosely packed than in γ -zirconium phosphate. An attempt has been made to exchange more interlayer HPO_4 groups of γ -zirconium phosphate with phenylphosphonate ions. However, no further exchanged product has been obtained.

According to the study of ion-exchange behavior,³ there are two kinds of hydrogen ions in γ -zirconium phosphate. When γ -zirconium phosphate is washed with sodium chloride solution, a half sodium ion-exchanged form $Zr(HPO_4)(NaPO_4) \cdot 1.5H_2O$ (called phase P) is obtained. Phase P is not reactive with any phosphoric ester or phenylphosphonic acid. Only the interlayer HPO_4^{2-} ions in the hydrogen form of γ -zirconium phosphate $Zr(HPO_4)_2 \cdot 2H_2O$ are exchangeable with ions having a $-PO_3$ group.

In the exchange with a homologous series of *n*-alkyl phosphate ions ($n-C_nH_{2n+1}PO_4^{2-}$, $1 \leq n \leq 18$),⁸ half of the HPO_4^{2-} ions were exchanged with the alkyl phosphate ions irrespective of the alkyl chain length. The study on the orientation of the alkyl chains between the phosphate layers revealed that the P–O bonds in the ester links were not perpendicular to the phosphate layers but inclined. In the reaction with phenylphosphonic acid, half of the HPO_4^{2-} ions are also exchanged with $C_6H_5OPO_3^{2-}$ ions.⁷ The amount exchanged with $C_6H_5OPO_3^{2-}$ ions is twice the amount exchanged with $C_6H_5PO_3^{2-}$ ions. It seems reasonable to assume that the phenyl groups of the interlayer $C_6H_5OPO_3^{2-}$ ions are inclined to the phosphate layers at the oxygen atoms of the ester links, whereas those of the interlayer $C_6H_5PO_3^{2-}$ ions are done directly at the phosphorus atoms of the P–C links. It seems likely

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that the interlayer HPO_4^{2-} ions adjacent to the exchange $\text{C}_6\text{H}_5\text{PO}_3^{2-}$ ions are much more subject to steric hindrance than those adjacent to the exchanged $\text{C}_6\text{H}_5\text{OPO}_3^{2-}$ ions. This may result in the exchange of one-fourth rather than half of the interlayer HPO_4^{2-} ions with $\text{C}_6\text{H}_5\text{PO}_3^{2-}$ ions. If the steric factor is predominant in determining the exchanged amount, it is reasonable to conclude that the exchanged $\text{C}_6\text{H}_5\text{PO}_3^{2-}$ ions can be ordered.

Acknowledgment. This study has been supported in part by a grant-in-aid of special research projects from The Ministry of Education of Japan. The authors wish to thank J. Shitaoka for electron microscopic measurements.

Registry No. $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, 13772-31-1; $\text{C}_6\text{H}_5\text{PO}_3^{2-}$, 16486-11-6; HPO_4^{2-} , 14066-19-4; $\text{Zr}(\text{C}_6\text{H}_5\text{PO}_3)_{0.5}(\text{HPO}_4)_{1.5} \cdot 2\text{H}_2\text{O}$, 76900-20-4.

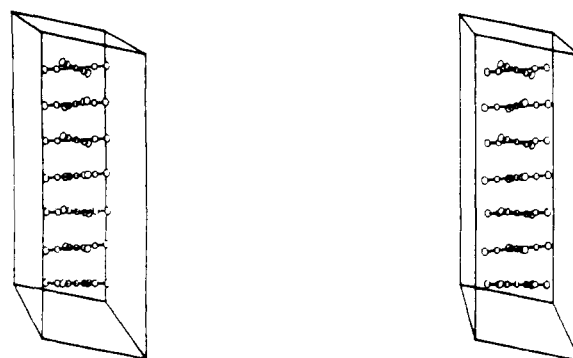


Figure 1. Stereoview into the narrow face (110) of a typical $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ crystal, showing a column of anions relative to the crystal morphology.

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Single-Crystal Polarized Specular-Reflectance Spectra of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$. A One-Dimensional Solid-State Effect

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and Robert M. Trapp, Jr.

Received July 30, 1980

Square-planar complexes of d^8 transition-metal ions have been of interest recently because of their unusual spectral and electrical properties.¹ Tetracyanoplatinates are especially dramatic examples, due to the brilliant colors of divalent salts²⁻⁴ and the metallic characteristics of mixed-valence salts,^{1,5,6} grown from colorless aqueous solutions. Tetracyanopalladate(II) salts have shown effects similar to those of the platinum(II) salts except the transitions are limited to the ultraviolet region and thus are not as noticeable.^{2,7} Doubt has been expressed, however, about such a "solid-state effect" being present in tetracyanonickelates.² Polarized absorbance studies of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ and other tetracyanonickelates⁸ have not observed solid-state effects of the same type found in the tetracyanoplatinates(II) and -palladates(II). A recent polarized specular reflection study involving $\text{BaK}_2[\text{Ni}(\text{C}-\text{N})_4]_2 \cdot 4\text{H}_2\text{O}$ ⁹ has shown that a strong solid-state effect is indeed observable in a tetracyanonickelate(II) salt. The purpose of this paper is to present polarized specular-reflectance spectra

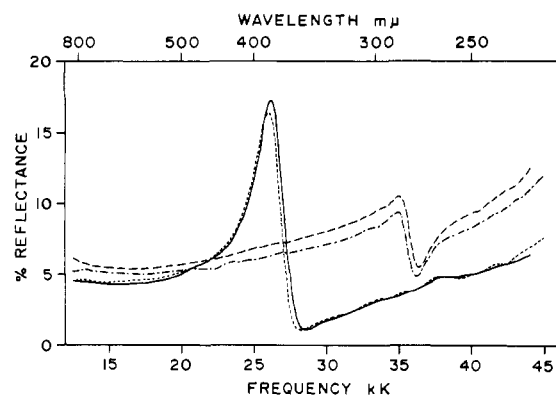


Figure 2. Polarized specular reflectance spectra of the (120) and (110) faces of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$. Parallel to c axis (out-of-plane): ---, (120); —, (110). Perpendicular to c axis (in-plane): - · - ·, (120); · · · ·, (110).

of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ which clearly demonstrate a strong (>7000) solid-state band and to compare this band with the solid-state bands reported for the isomorphous analogues $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ and $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$. The trend observed supports the view that the same effect is operating in this tetracyanonickelate as in the tetracyanopalladate and -platinates salts.

Experimental Section

$\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ was prepared by the addition of excess BaCl_2 to $\text{K}_2\text{Ni}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$, followed by evaporation and recrystallization. Slow evaporation of aqueous solutions of this product yielded well-formed clear yellow-orange crystals $\sim 1 \times 0.6 \times 2$ mm, with highly planar surfaces suitable for specular reflection. The crystals were maintained in an atmosphere of 84% relative humidity at room temperature to avoid loss of waters of hydration.

Anal. Calcd for $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$: Ba, 36.90; Ni, 15.80; C, 12.90; N, 15.10; O, 17.20; H, 2.20. Found: Ba, 36.73; Ni, 16.01; C, 12.78; N, 15.10; O, 17.02; H, 2.19; K, <0.02 .¹⁰

Polarized reflection spectra were obtained on a microspectrophotometer described in detail elsewhere.¹¹ Measurements were made relative to an aluminum mirror and corrected for aluminum reflectivity.¹² Spectra were obtained with the electric vector aligned parallel (\parallel) and perpendicular (\perp) to the elongation axis of the crystal, on the (120) and (110) faces of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$. For each face, measured on different sets of crystals, six of the best reflection spectra were averaged.¹³ The reflectance data were transformed into absorption-equivalent spectra through Kramers-Kronig analyses.¹⁴ The

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