

HClO<sub>4</sub>) show that the absorbance of both the mixtures slightly decreases as compared to that of Ag<sup>+</sup>. Absorbance of  $1 \times 10^{-4}$  M [Ag<sup>+</sup>] with different concentrations of H<sub>3</sub>PO<sub>2</sub> and H<sub>3</sub>PO<sub>3</sub> at 202 and 206 nm, respectively, were measured at 30 °C, and the formation constant for the 1:1 complex was calculated by the method of Ramette.<sup>15</sup> The formation constants for H<sub>3</sub>PO<sub>2</sub> and H<sub>3</sub>PO<sub>3</sub> with the assumption of a 1:1 complex were found to be  $138 \pm 19$  and  $510 \pm 30$  M<sup>-1</sup>, respectively.

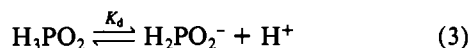
**pH Measurements.** Titration of 0.05 M [H<sub>3</sub>PO<sub>2</sub>] with and without 0.0025 M [Ag<sup>+</sup>] against 0.11 M [NaOH] indicated complex formation, but the stability constants could not be determined.

### Discussion

The kinetics and spectrophotometric results of the present work indicate complex formation between Ag<sup>+</sup> and H<sub>3</sub>PO<sub>2</sub> (eq 2). This is in line with the coordinating properties of H<sub>3</sub>PO<sub>2</sub>



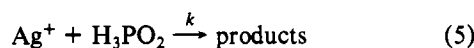
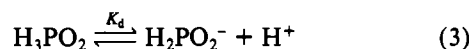
with other metal ions<sup>16</sup> with concentration equilibrium constants between 150 and 10. Important observations from the mechanistic point of view are the limiting rates at high [H<sup>+</sup>] and high [Ag(I)] and the dependence of the rate on their relative values. Mixed up with this is the question of free concentration of H<sub>3</sub>PO<sub>2</sub> which is controlled by the dissociation equilibrium (eq 3), with a  $K_d$  value<sup>13</sup> of 0.135 at 25 °C and



$I = 1.0$  M and the complex formation equilibrium (2). Two things are further to be noted. (1) At high [H<sup>+</sup>],  $v/[\text{H}_3\text{PO}_2][\text{Ag}^+]$  gives a constant value of  $0.104 \pm 0.004$  M<sup>-1</sup> s<sup>-1</sup>. (2) At low [H<sup>+</sup>] or at high [Ag<sup>+</sup>],  $v/[\text{H}_3\text{PO}_2][\text{H}^+]$  gives a constant value of  $(4.27 \pm 0.12) \times 10^{-3}$  M<sup>-1</sup>. This would imply a rate law of the form in eq 4, where  $A$ ,  $B$ , and  $C$  are

$$v = -d[\text{Ag(I)}]/dt = \frac{A[\text{H}_3\text{PO}_2][\text{H}^+][\text{Ag}^+]}{B[\text{Ag}^+] + C[\text{H}^+]} \quad (4)$$

constants. Considering one situation for a simple reaction between Ag<sup>+</sup> and H<sub>3</sub>PO<sub>2</sub>, the mechanism and the rate law are given by



Hence

$$v = -d[\text{Ag(I)}]/dt = \frac{2k[\text{H}_3\text{PO}_2][\text{Ag}^+][\text{H}^+]}{[\text{H}^+] + K_d + K_d K_1 [\text{Ag}^+]} \quad (6)$$

If at high [H<sup>+</sup>] ( $\approx 1.0$  M)  $K_d + K_d K_1 [\text{Ag}^+]$  could be neglected, the rate law reduces to eq 7. The value of  $k$  is  $(5.2 \pm 0.2)$

$$v = 2k[\text{H}_3\text{PO}_2][\text{Ag}^+] \quad (7)$$

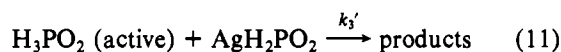
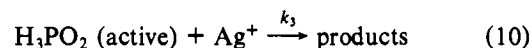
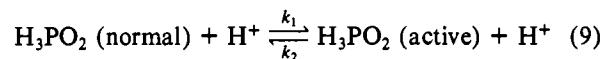
$\times 10^{-2}$  M<sup>-1</sup> s<sup>-1</sup>. Similarly if at low [H<sup>+</sup>],  $[\text{H}^+] + K_d$  could be neglected as compared to  $K_d K_1 [\text{Ag}^+]$  (which is not very true), the rate law reduces to eq 8. The value of  $k$  using  $K_d$

$$v = \frac{2k[\text{H}_3\text{PO}_2][\text{H}^+]}{K_d K_1} \quad (8)$$

$= 0.124$  and  $K = 138$  was found to be  $3.65 \times 10^{-2}$  M<sup>-1</sup> s<sup>-1</sup>. The two values are fairly similar. The value of  $4.27 \times 10^{-3}$  M<sup>-1</sup> s<sup>-1</sup> at 30 °C is comparable to the value  $1.3 \times 10^{-3}$  M<sup>-1</sup> s<sup>-1</sup> at 25 °C reported by Mitchell.<sup>2</sup>

One more way to test rate law 6 is to plot  $1/v$  vs.  $1/[\text{H}^+]$ . From the slope:intercept ratio, the values of  $K_d(1 + K_1[\text{Ag}^+])$  can be calculated, and from the  $K_d$  value of 0.124, the value of  $K_1$  was found to be  $170 \pm 44$  M<sup>-1</sup>. The order of magnitude of  $K_1$  is the same as determined spectrophotometrically.

Another way to explain these results is to assume the much talked about tautomeric equilibrium<sup>7</sup> through mechanism (9)–(11). This would lead to rate law 12. The verification



$$v = \left( \frac{2k_1 k_3 [\text{Ag}^+][\text{H}_3\text{PO}_2][\text{H}^+]}{k_3 [\text{Ag}^+] + k_2 [\text{H}^+]} + \frac{2k_1 k_3' [\text{AgH}_2\text{PO}_2][\text{H}_3\text{PO}_2][\text{H}^+]}{k_3' [\text{AgH}_2\text{PO}_2] + k_2 [\text{H}^+]} \right) \left( \frac{[\text{H}^+]}{[\text{H}^+] + K_d} \right) \quad (12)$$

of this rate law is still more difficult, and it can be tested only qualitatively by reducing the rate law under different limiting conditions. Different ionic strength effects and different overall energies of activation under two different conditions of relative concentrations of Ag<sup>+</sup> and H<sub>3</sub>PO<sub>2</sub> clearly show that the reactive species are different under the two conditions. The increase in the rate in the presence of phosphorous acid supports the facts of reactive free H<sub>3</sub>PO<sub>2</sub> and the complexing of Ag<sup>+</sup> with H<sub>3</sub>PO<sub>2</sub>.

**Acknowledgment.** A.K.I. is thankful to M. D. College, Sri Ganganagar for the study leave, and the UGC for providing the finances and the fellowship to carry out this work.

**Registry No.** H<sub>3</sub>PO<sub>2</sub>, 6303-21-5; Ag<sup>+</sup>, 14701-21-4.

**Supplementary Material Available:** Initial rates at temperatures of 35, 40, and 45 °C under two different conditions, absorption data of mixtures of Ag<sup>+</sup> and H<sub>3</sub>PO<sub>2</sub> and of Ag<sup>+</sup> and H<sub>3</sub>PO<sub>3</sub>, values of constants under two limiting conditions of eq 4, and the values of  $K_1$  from kinetics results (5 pages). Ordering information is given on any current masthead page.

Contribution from The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan

### Synthesis and Characterization of a New Layered Compound, V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub>

S. Son, R. Kanno, and M. Koizumi\*

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Many layered inorganic compounds are known to act as host lattices and react with a variety of guest atoms or molecules to give intercalation compounds in which the guest is inserted between the host layers. Recently these materials have attracted considerable attention for such different reasons as the observation that the superconducting transition temperature of some hosts increases on intercalation of amines<sup>1</sup> and the

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use of alkali-metal intercalation reactions such as Li/TiS<sub>2</sub> in secondary battery systems.<sup>2</sup> In this paper, we report the preparation and characterization of a new layered compound in which an alkali metal can be intercalated.

### Experimental Section

**Materials and Preparations.** Reagent grade thioacetic acid and VOCl<sub>2</sub> were purchased from Nakarai Chemicals Ltd. Solid VOCl<sub>2</sub> was crushed to a powder in a drybox before use. A 3-mmol sample of VOCl<sub>2</sub> and 2 mL of thioacetic acid were put into a 20-mL heavy-walled Pyrex tube equipped with a screw cap, and the mixture was allowed to warm to 60 °C. After 2 days dark brown platelike crystals were formed. They were separated from the mother liquor by filtration, washed with water and benzene, and finally dried under vacuum. After 2 days reaction we obtained large as-grown platelike single crystals in about 60% yield. It seems that the higher yields depend on time duration for the growing of crystals. Anal. Calcd for V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub>: C, 16.14; H, 2.02; S, 64.70; V, 17.13. Found: C, 16.05; H, 1.97; S, 64.31; V, 17.23.

The butyllithium (*n*-C<sub>4</sub>H<sub>9</sub>Li) was purchased from Nakarai Chemicals Ltd. as a 1.6 M solution in hexane. To prepare the lithium-intercalated complex, it was necessary to react V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub> with about a 50% mol excess of butyllithium (diluted to about 0.2 M with hexane) for 1 day at 60 °C in a 20-mL heavy-walled Pyrex tube equipped with a screw cap. The product was filtered, washed with hexane several times, and finally dried under vacuum.

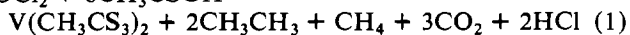
**Measurements.** X-ray powder diffraction data was obtained with the use of a Rigaku-Denki diffractometer and Ni-filtered Cu K $\alpha$  radiation. Chemical analysis of the compound was made with use of standard techniques. Differential thermogravimetric analysis was conducted by using a Rigaku-Denki unit programmed for a heating rate of 10 °C/min. The infrared spectrum in the region 4000–700 cm<sup>-1</sup> was observed on a Hitachi-Perkin-Elmer spectrophotometer fitted with a sodium chloride prism. Samples were dispersed in potassium bromide disks. The magnetic susceptibilities were determined by the Faraday method with use of a magnetic field of 10000 G. The measurement was conducted in the temperature region between 80 and 300 K. The temperature calibration of the equipment was obtained by the measurement of the magnetic susceptibility of FeSO<sub>4</sub>(N-H<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O.

**X-ray Crystallography.** A platelike crystal of approximate dimension 0.25 × 0.10 × 0.20 mm was mounted on the end of a thin-glass fiber. Cell dimensions were obtained from Weissenberg photographs using zirconium-filtered Mo K $\alpha$  radiation ( $\lambda = 0.7107$  Å). Weissenberg photographs indicated that the crystals belonged to the monoclinic system with space group *P*2<sub>1</sub>/*c*. The cell constants were found to be *a* = 10.412 Å, *b* = 11.191 Å, *c* = 9.062 Å, and  $\beta = 96.6^\circ$ . The unit cell volume of 1048.6 Å<sup>3</sup> with four formula units per unit cell gives a density of 1.88 g/cm<sup>3</sup> which is in good agreement with the measured density of 1.87 g/cm<sup>3</sup> calculated by the flotation method.

### Results and Discussion

Chemical analysis data indicated that this new layered compound had the chemical formula V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub>. V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub> was very stable to both strong acids and bases. A solvent to dissolve this compound is not known at present time.

The reaction process of VOCl<sub>2</sub> and thioacetic acid has not been established with certainty. However, eq 1 could be VOCl<sub>2</sub> + 6CH<sub>3</sub>CSOH →



suggested since the evolution of carbon dioxide and hydrochloride were indicated. This postulate suggests that the thioacetic acid might be decomposed and reacted with VOCl<sub>2</sub>. During the reaction, it was recognized that solid VOCl<sub>2</sub> was completely dissolved and the clear solution of thioacetic acid turned dark brown. When crystals of V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub> were not finely powdered, the X-ray diffraction pattern of the sample showed strongly preferred orientation peaks of the (*h*00) reflections, a fact characteristic of layered compounds. An X-ray powder diffraction pattern of V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub> which was com-

Table I. Vibration Frequencies (cm<sup>-1</sup>) of V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub>

		assignment
1350	vw	$\delta$ (CH <sub>3</sub> )
1165	s	$\nu$ (CS)
1145	vs	$\nu$ (C-C)
867	vs	$\nu$ (CS)

Table II. X-ray Powder Data for V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub>

<i>hkl</i>	<i>d</i> <sub>obsd</sub> , Å	<i>d</i> <sub>calcd</sub> , Å	<i>I</i>
100	10.394	10.34	100
100	7.622	7.595	20
011	7.025	7.014	60
-111	6.014	6.062	70
020	5.604	5.595	30
200	5.181	5.171	5
210	4.950	4.964	15
002	4.548	4.501	15
-121	4.414	4.421	20
121	4.227	4.222	20
220	3.799	3.797	5
300, 130	3.456	3.447	10
310	3.252	3.294	5
013	3.097	2.898	15
140, 040	2.720	2.700	20
041	2.597	2.671	5
410	2.530	2.519	15
004	2.279	2.250	20
150	2.070	2.187	15
060	1.875	1.865	5

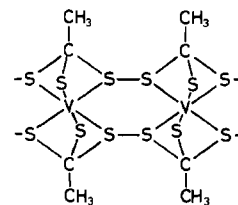


Figure 1. A proposed unit structure of a layered polymer of V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub>.

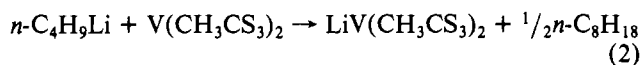
pletely crushed into powdered form, could be indexed on the basis of a monoclinic unit cell with the previously reported cell constants. The indexing and observed and calculated *d* spacings are given in Table I. As described in the Experimental Section, this new layered compound belongs to the monoclinic system with space group of *P*2<sub>1</sub>/*c* (*Z* = 4). At the present stage, a proposed bond structure of the V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub> was drawn as shown in Figure 1 from the crystal data and the chemical formula. In order to confirm this structural speculation, however, it is necessary to determine the crystal structure by X-ray analysis.

In the infrared spectrum of V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub>, some characteristic vibrations of the C-S, C-C and C-H bonding were observed as shown in Table II. These infrared results indicated that the CH<sub>3</sub> group and S atoms were attached to C atoms. Thermal analysis data of V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub> showed that the compound decomposed at 220 °C, associated with 69% weight loss. The sample cooled from 500 °C was identified to be V<sub>2</sub>O<sub>5</sub> by X-ray diffractometry. From the measurement of the magnetic susceptibility, the V(CH<sub>3</sub>CS<sub>3</sub>)<sub>2</sub> complex was found to be diamagnetic. This result indicates that vanadium is in the pentavalent state.

The formation process of the lithium-intercalated complex of the present system might be thought to be the same as that of the reaction of *n*-butyllithium with the layered transition-metal dichalcogenides.<sup>3</sup> The present reaction was expressed by eq 2. After the reaction many cracks parallel to the host

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(3) M. B. Dines, *Mater. Res. Bull.*, **10**, 287 (1975).



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  $\text{cm}^{-1}$  were attributed to the vibrations of the  $\text{H}_2\text{O}$  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;  $\text{VOCl}_2$ , 10213-09-9;  $\text{CH}_3\text{CSOH}$ , 507-09-5; *n*- $\text{C}_4\text{H}_9\text{Li}$ , 109-72-8.

Contribution from the Department of Applied Chemistry,  
Faculty of Engineering, Hiroshima University,  
Hiroshima 730, Japan

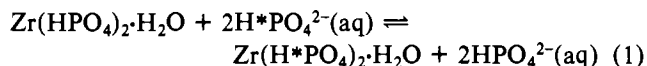
### Exchange of Interlayer Hydrogen Orthophosphate Ions of Zirconium Bis(hydrogen orthophosphate) Dihydrate with Phenylphosphonate Ions

Shoji Yamanaka\* and Makoto Hattori

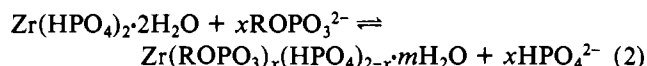
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Zirconium bis(hydrogen orthophosphate) is an insoluble ion exchanger with layer structure. The mono- and dihydrate,  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  and  $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ , are known, which are called  $\alpha$ - and  $\gamma$ -zirconium phosphate, respectively.<sup>1-3</sup> Water molecules reside between the layers. Both forms consist of  $\text{ZrO}_6$  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  $\text{ZrO}_6$  octahedra. In the structure of  $\gamma$  form, these octahedra and tetrahedra are more densely linked than those of the  $\alpha$  form.<sup>3,4</sup>

Rahman and Barrett<sup>5,6</sup> investigated the exchange of phosphate ions of  $\alpha$ -zirconium phosphate in aqueous solutions using  $^{32}\text{P}$  isotope in a heterogeneous system. They have reported that phosphate groups of internal as well as outer surfaces of  $\alpha$ -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  $^{32}\text{P}$  isotope.



In a series of previous studies,<sup>7,8</sup> we have reported that the interlayer  $\text{HPO}_4^{2-}$  ions of  $\gamma$ -zirconium phosphate can be reversibly exchanged with various orthophosphoric ester ions of the type  $\text{ROPO}_3^{2-}$  when  $\gamma$ -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  $\text{HPO}_4^{2-}$  ions of  $\gamma$ -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.<sup>7</sup>  $\gamma$ -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  $\text{Na}_2\text{CO}_3$ - $\text{K}_2\text{CO}_3$  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%  $\text{Na}_2\text{CO}_3$  solution and 50 mL of 1 M  $\text{NH}_3$ . The zirconium content was determined gravimetrically by ignition of the residue to  $\text{ZrO}_2$ . The filtrate together with the washings was used to determine the phosphorus content by the colorimetric method of Bernheit and Wreath.<sup>9</sup>

### Results and Discussion

The basal spacing of  $\gamma$ -zirconium phosphate was enlarged from 12.27 to 15.14 Å by the refluxing. Electron microscopic examination showed that the size of the initial  $\gamma$ -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  $\gamma$ -zirconium phosphate shown previously.<sup>3</sup> These results indicate

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