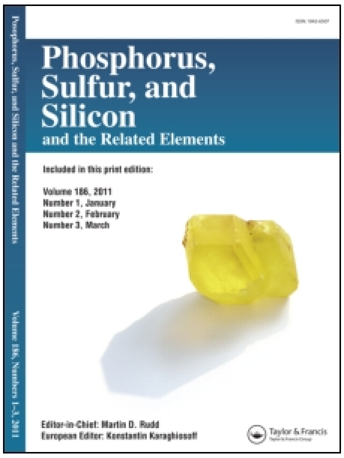

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Intercalation of Pyridine and Picolines to $WO(P_2O_7)$

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ABSTRACT Pyridine and picoline complexes of $WO(P_2O_7)$ were prepared by direct intercalation and ion exchange. The systematic change of the basal spacings of the complexes where γ-picoline gives the largest value indicates monolayer arrangement of perpendicular molecules in the interlamellar spaces.

INTRODUCTION

The tungsten pyrophosphate [$WO(P_2O_7)$] has a layered structure which is composed of WO_6 octahedra and P_2O_7 groups linked by corner sharing (1). The layers are stacked along the a-axis of a monoclinic cell and the basal spacing was found to expand by intercalation of inorganic and organic cations as well as neutral n-alkylamine molecules(2,3). Neat n-alkylamines were reacted directly with $WO(P_2O_7)$ at room temperature and taken up as neutral molecules, the host layer remaining not reduced (3). On the other hand pyridine has been reported to react directly with inorganic layered compounds without protons in the structure to form reduced intercalation compounds or grafted compounds (4,5). The formation of pyridine and picoline complexes of $WO(P_2O_7)$ by intercalation and ion exchange is described here.

EXPERIMENTAL

Powders of WO_3 and $(NH_4)_2HPO_4$ were mixed in a molar ratio of 1:5, heated at *ca.* 250 °C and successively calcined at 650 °C for 4 d. in a gold boat. The product was washed with distilled water, dried and ground. The ground powder was used as a starting material for intercalation. $Na_xWO(P_2O_7){\cdot}nH_2O$ ($x \approx 1.4$) and $Sn_xH_yWO(P_2O_7){\cdot}nH_2O$ ($2x+y \approx 0.7$) were prepared by reducing with 0.1 M aqueous solution of $Na_2S_2O_4$ at 60 °C for 1d. and 0.2 M HCl solution of $SnCl_2$ at room temperature for 3d. Ion exchange of these intercalation compounds with pyridinium ion and its derivatives was carried out by using 0.2 M aqueous solutions of chlorides at 60 °C for a week. Neat pyridine and its derivatives was reacted with $WO(P_2O_7)$ at 180 °C for several days in a sealed glass tube. Anhydrous condition was kept during the whole process, but finally it was found that moisture did not affect substantially the reaction and water molecules were only taken up into the interlayer spaces.

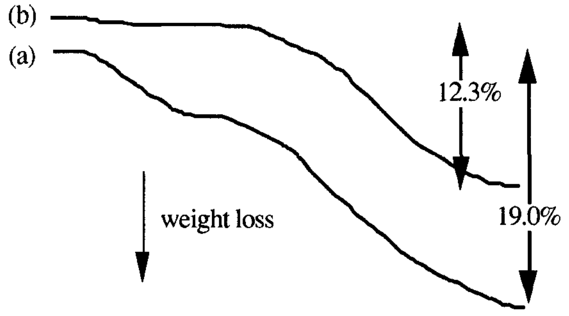

Fig. 1. TG curves of pyridine complexes
(a) as-prepared
(b) dried in vacuum

X-ray powder pattern was taken by using a diffractometer with Ni-filtered CuKα radiation and a scanning speed of 2°/min. The basal spacing of samples dried at 100°C in vacuum overnight was also measured. TG-DTA measurement was carried out with a heating rate of 10°C/min. Amount of organic molecules taken up was determined by the elemental analysis and TG measurement. IR spectrum was recorded by the KBr method.

RESULTS and DISCUSSION

By the reaction with pyridine and picolines large expansion of the starting powders was observed, accompanying color change to green. The basal spacing increased from 7.7 to 12.7 Å on the reaction with pyridine. From the elemental analysis and TG measurement the ratio of pyridine/W was found to be 0.70. Under the existence of small amount of water during the reaction more pyridine and water molecules were incorporated. However the basal spacing of the product was as large as the product prepared anhydrous condition. The TG curves of the products are shown in Fig. 1. Accompanying endothermic peaks in DTA curve, a large weight loss was observed above 200 °C in TG curve, although the as-prepared sample (a) showed another gradual weight loss from about 50 °C. The weigh loss at lower temperature is attributed to removal of part of pyridine and water. The ratios of pyridine/W and H_2O/W of the hydrated sample were 0.92 and 1.25, respectively. The amount of pyridine in the dried sample was almost corresponding to that of the product prepared anhydrous condition.

As indicated by the change of color, tungsten was thought to be reduced upon the reaction and W^{5+}/W ratio was determined to be 0.69, coinciding with the ratio of pyridine/W for the product prepared under anhydrous condition and dried sample. Therefore pyridine molecules intercalated into the interlayer spaces of $WO(P_2O_7)$ are considered to exist as

Table 1. The basal spacings of pyridine and picolines complexes of WO(P2O7)

molecule	basal spacing (Å) (hydrated)	basal spacing (Å) (anhydrous)
pyridine	-	12.7
γ-picoline	-	12.7
β-picoline	-	13.2
α-picoline	-	14.4
pyridine*	13.3	12.6
pyridine**	13.6	12.8

* from $Na_xWO(P_2O_7)\cdot nH_2O$
** from $Sn_xH_yWO(P_2O_7)\cdot nH_2O$

pyridinium ions and weakly bonded part of pyridine in the hydrated sample is probably neutral. In fact the IR spectrum of the product exhibited an clear absorption at 1540 cm^{-1}, indicating existence of protonated pyridine (6). An attempt of ion exchange of pyridinium ion with proton was carried out in acid medium at room temperature and resulted in the formation of $H_xWO(P_2O_7)\cdot nH_2O$ (2). The reaction scheme for the generation of negative layer charges is given by Schöllhorn et. al (4).

By ion exchange with pyridinium ion pyridine complexes of $WO(P_2O_7)$ were also prepared from $Na_xWO(P_2O_7)\cdot nH_2O$ and $Sn_xH_yWO(P_2O_7)\cdot nH_2O$. However in the case of $Na_xWO(P_2O_7)\cdot nH_2O$ small amount of the starting material remained unchanged. The ratios of pyridine/W were determined to be 0.5 for the product from $Na_xWO(P_2O_7)\cdot nH_2O$ and 0.41 from $Sn_xH_yWO(P_2O_7)\cdot nH_2O$, respectively. The basal spacings of theion exchanged products were 13.3 and 13.6 Å, but those were reduced to 12.6 and 12.8 Å by drying.

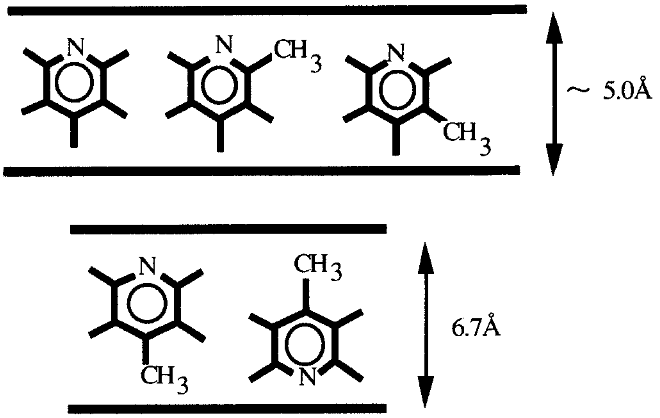

Fig. 2. Possible arrangement of pyridine and picolines in the interlayer spaces of $WO(P_2O_7)$

As shown in Table 1, systematic changes of the basal spacing were observed for pyridine and picolines, depending on the position of methyl groups. Among pyridine and picoline complexes γ-picoline complex has the largest basal spacing, while the others have almost constant basal spacings. Complexes of pyridine and picolines have been reported for tantalum disulfide and hydrogen molybdenum bronze and their basal spacing are almost independent on the position of methyl group (7, 8), while similar behavior to $WO(P_2O_7)$ was observed for $HTaWO_6$, FeOCl and $HTiNbO_5$ where γ-picoline complex have the maximum basal spacing (9-11). Then similar monolayer arrangement of perpendicular molecules in the interlamellar spaces is conceivable for the complexes of $WO(P_2O_7)$, because the systematic change of the basal spacing can be explained well by supposing that the protonated nitrogen atom is directed toward the layer to maximize the interaction between the molecule and the layer as shown in Fig. 2. By this configuration the 4-position derivative gives the largest basal spacing; this is as observed. Contrary to this, the guest-guest interaction may prevail, when the expansion of basal spacing almost does not vary with the position of the functional groups, as observed for hydrogen molybdenum bronze (8). Because the expansion of the complexes of $WO(P_2O_7)$ are slightly smaller than the size of organic molecules in the interlayer spaces, the molecules might be nesting into the layer or tilted in respect to the layer.

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