Intercalation Compounds of (Diphosphato)oxotungsten(VI), [WO(P_2O_7)]

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Reduction of [WO(P_2O_7)] in aqueous solution with strong reducing agents results in the uptake of cations and water molecules in the interlayer spaces and expansion of the basal spacing. The product $Na_xWO(P_2O_7)\cdot nH_2O$ ($0.80 \leqslant x \leqslant 1.41$) was produced with $Na_2S_2O_4$ solution. At $x > 1.1$ a hydrated phase with a basal spacing of 10.8 Å and $n = 1.0$ was obtained, and at $x < 1.1$ three hydrated states with basal spacings of 11.5, 10.8, and 10.4 Å were found, depending on the humidity. The basal spacing of the unhydrated phase is 9.5 Å at any value of x. Upon reduction with acidified $SnCl_2$ solution, Sn^{2+} and H^+ were taken up into the interlayer spaces to form $Sn^{2+}{}_xH_yWO(P_2O_7)\cdot nH_2O$ with a basal spacing of 12.2 Å. The sum $(2x + y)$ ranged from 0.46 to 0.80.

Transition-metal compounds with neutrally charged layers such as dichalcogenides and MoO_3 are known to form intercalation compounds upon electrical or chemical reduction.[1–4] Cations to balance the negative charges generated on the host layers and very often solvent molecules are taken up into the interlayer spaces. The reversibility of the topotactic reactions is of potential use for electrode materials.[5]

An advantage of these compounds is that the average surface area per cation in the interlayer spaces can be controlled fairly easily by regulating the degree of reduction. Contrary to the generation of negative charge on the electrically neutral layer, the area per cation can also be controlled by substitution of cations forming negatively charged layers by cations bearing higher charges and then reducing the number of cations in the interlayer spaces. However, the homogeneity range of such solid solutions is rather limited, and the average area per charge cannot be varied widely. For example, in the system $K_{1-x}(Ti_{1-x}Nb_{1+x})O_5$ the maximum solid solubility is $x = 0.15$.[6]

The tungsten pyrophosphate [WO(P_2O_7)] is known to have a layered structure.[7] The layers are built up from corner sharing of WO_6 octahedra and P_2O_7 groups and are stacked along the *a* axis of a monoclinic cell. They are considered to be held together by van der Waals forces, since they are electrically neutral. We now describe here the formation of intercalation compounds, $A_xH_yWO(P_2O_7)\cdot nH_2O$ (A = Na or Sn), by reduction of [WO(P_2O_7)] in aqueous solutions.

Experimental

Preparation of [WO(P_2O_7)].—Powders of WO_3 and $[NH_4]_2[HPO_4]$ were mixed in a molar ratio of 1:5, heated at *ca.* 250 °C in a gold boat to decompose the ammonium phosphate, and finally calcined at 650 °C for 4 d. The product was washed with distilled water. The transparent thin rectangular crystals showed an identical *X*-ray powder diffraction pattern to that given in the literature.[7] The crystals were ground and used as a starting material.

Reduction of [WO(P_2O_7)] *with Aqueous* $Na_2S_2O_4$.—Powdered [WO(P_2O_7)] (2 g) was suspended in an aqueous solution of $Na_2S_2O_4$ at room temperature (*ca.* 10 °C) or 90 °C for periods of a few hours to 1 week. The concentration of $Na_2S_2O_4$ ranged from 0.1 to 1 mol dm^{-3}. The product was washed several times with distilled water and dried in air.

Reduction of [WO(P_2O_7)] *with Aqueous* $SnCl_2$.—Solutions of $SnCl_2$ (0.1 mol dm^{-3}) were prepared by dissolving $SnCl_2\cdot2H_2O$ in 4 and 6 mol dm^{-3} HCl solutions. Powdered [WO(P_2O_7)] (2 g) was added to the solution and the suspension stirred at room temperature or 30 °C for up to 48 h. The product was filtered off, washed several times with 1 mol dm^{-3} HCl solution, and dried in air.

Ion exchange with H^+ was carried out for both intercalated compounds prepared in $Na_2S_2O_4$ and $SnCl_2$ solutions, using 1 mol dm^{-3} HCl solution at room temperature.

Characterization.—*X*-Ray powder diffraction patterns were taken by using a Rigaku-Denki 2013 diffractometer with nickel-filtered Cu-K_α radiation. The patterns for the intercalated compounds could not be indexed with a monoclinic cell, unlike [WO(P_2O_7)]. The intercalation is considered to cause not only expansion of basal spacings but also deformation of the host layer probably to a triclinic cell. Changes of basal spacings after the intercalation were calculated from the reflections for the basal planes, *h*00, up to around $2\theta = 50°$.

Sample compositions were determined by thermogravimetry and chemical analysis. The samples were dissolved in HF–HNO_3 solution. Sodium was analysed by atomic absorption spectrometry. Tin was determined by precipitation as sulphide and calcination to SnO_2. The tin released on exchange with H^+ was precipitated with cupferron. The amounts of tin in the interlayer spaces and that released on exchange were found to be almost coincident. The mean oxidation state of tungsten was determined by titration with cerium(IV) sulphate. The samples were added to standardized cerium(IV) solution in 3 mol dm^{-3} H_2SO_4 and oxidized to W^{6+} with stirring. The excess of Ce^{4+} was titrated with standard iron(II) solution.

The dependence of the basal spacing on relative humidity was examined by storing samples over constant-humidity reagents until constant weight was reached. The reagents were P_2O_5, $ZnCl_2\cdot0.5H_2O$, $CaCl_2\cdot6H_2O$, $K_2CO_3\cdot2H_2O$, $NaBr\cdot2H_2O$, and $Na_2CO_3\cdot10H_2O$, having relative humidities of *ca.* 0, 10, 32, 43, 58, and 87%, respectively.[8]

Reverse reactions (oxidation of the intercalated compounds) were carried out with solutions of 0.1 mol dm^{-3} $KMnO_4$ and 30% H_2O_2 at room temperature.

Results

Representatives of the intercalated compounds formed are shown in Table 1.

Intercalation Compounds, $Na_xWO(P_2O_7)\cdot nH_2O$.—The colour of powdered [WO(P_2O_7)] changed to greenish gold

Table 1. Products obtained by reducing [$WO(P_2O_7)$] in $Na_2S_2O_4$ or $SnCl_2$ solutions; r.t. = room temperature

	Preparative condition			
Composition	Duration (h)	Temperature (°C)	Concentration of reducing agent (mol dm^{-3})[a]	Basal spacing (Å)[b]
Sodium type				
$Na_{1.41}WO(P_2O_7)\cdot1.0H_2O$	24	90	1.0	10.8
$Na_{1.23}WO(P_2O_7)\cdot1.1H_2O$	24	90	0.5	10.8
$Na_{1.12}WO(P_2O_7)\cdot1.0H_2O$	24	r.t.	0.5	10.8
$Na_{1.08}WO(P_2O_7)\cdot1.4H_2O$	6	r.t.	0.2	11.5
$Na_{1.03}WO(P_2O_7)\cdot1.2H_2O$	3	r.t.	0.5	11.5
$Na_{0.80}WO(P_2O_7)\cdot1.5H_2O$[c]	3	r.t.	0.2	11.5
SnH type				
$Sn_{0.16}H_{0.14}WO(P_2O_7)\cdot2.0H_2O$	16	r.t.	4, 0.1	12.2
$Sn_{0.15}H_{0.27}WO(P_2O_7)\cdot1.9H_2O$	43	r.t.	4, 0.1	12.2
$Sn_{0.08}H_{0.63}WO(P_2O_7)\cdot1.5H_2O$	22	30	4, 0.1	12.2
$Sn_{0.09}H_{0.62}WO(P_2O_7)\cdot1.7H_2O$	48	30	4, 0.1	12.2
$Sn_{0.16}H_{0.36}WO(P_2O_7)\cdot1.6H_2O$	22	30	6, 0.1	12.2

[a] Concentrations of HCl and $SnCl_2$ solutions respectively are indicated for SnH type. [b] Values for the most hydrated phases are shown. [c] Flakes of [$WO(P_2O_7)$] were used as a starting material.

Table 2. Variation of the basal spacing and amount of water with humidity

	Relative humidity (%)					
Compound	87	58	43	32	10	*ca.* 0
$Na_{1.08}WO(P_2O_7)\cdot nH_2O$						
Basal spacing (Å)	11.5	11.5	10.8	10.4	10.4	9.5
Amount of water (n)	—	1.2	1.1	0.9	0.9	*ca.* 0
$Sn_{0.18}H_{0.18}WO(P_2O_7)\cdot nH_2O$						
Basal spacing (Å)	12.2	12.2	12.1 (10.6)*	12.1 (10.6)*	10.6	10.5
Amount of water (n)	2.3	1.9	1.3	1.1	0.8	0.2
$H_{0.54}WO(P_2O_7)\cdot nH_2O$						
Basal spacing (Å)	12.2	12.2	12.2	12.2	12.2 (11.5)*	12.2 (11.5)*
Amount of water (n)	1.9	1.7	1.4	1.2	0.8	0.2

* Value for minor phase.

when reduced extensively or to dark green when reduced less extensively in $Na_2S_2O_4$ solutions and an expansion of the basal spacing was observed. The amount of Na^+ taken up in the interlayer spaces agreed with the amount of positive charge expected from the mean oxidation state of W. The composition of the products was found to be $Na_xWO(P_2O_7)\cdot nH_2O$ (denoted as the sodium type hereafter).

Two series of hydrated phases were observed for the sodium type, depending on the degree of reduction. The basal spacings of the most hydrated state in each series were determined to be 10.8 and 11.5 Å. The 10.8-Å phase which was obtained at 90 °C or/and after a long time is the more reduced phase, containing more Na^+ ions than the 11.5-Å phase. The boundary between these two phases seems to be located around $x = 1.1$, where x ranged from 1.41 to 0.80 in this type. The average number of water molecules in the interlayer spaces of the 10.8-Å phase was estimated to be $n = 1.0$. The basal spacing of 10.8 Å was maintained upon drying over P_2O_5, but decreased to 9.5 Å upon heating at 90 °C in air. No other basal spacing was observed in the course of dehydration.

The 11.5-Å phase can accommodate more water (n *ca.* 1.2) than the 10.8-Å phase, but loses it easily. The basal spacing of this phase decreased to 9.5 Å upon drying over P_2O_5. The dependence of the basal spacing on relative humidity is shown in Table 2. Since phases with basal spacings of 10.8 and 10.4 Å were observed as single phases, they seem each to have stable humidity ranges. The number of water molecules for these two states was estimated to be about 1.1 and 0.9, respectively.

Thermogravimetric analysis (t.g.a.) curves for the sodium type product are shown in Figure (*a*) and (*b*). The weight increased upon oxidation of the sample at about 500 °C, and then decreased upon dehydration at *ca.* 110 °C. The basal spacing of 9.5 Å observed for the dehydrated state of the 10.8- and 11.5-Å phases is reasonable, if the basal spacing for [$WO(P_2O_7)$] of 7.67 Å and ionic radius of Na^+ are taken into account.

Intercalation Compounds, $Sn_xH_yWO(P_2O_7)\cdot nH_2O$.—A dark blue powder was obtained by treatment of [$WO(P_2O_7)$] with $SnCl_2$ solution. Chemical analysis showed that the amount of Sn in the products was much less than that required from the mean oxidation state of W. The chemical formula of the products is $Sn_xH_yWO(P_2O_7)\cdot nH_2O$, containing Sn as Sn^{2+} and denoted the SnH type. The t.g.a. curve for this compound is shown in Figure (*d*). The second step of weight loss is comparable to the weight loss expected for removal of protons

Table 3. Areas per charge for layered oxides

Compound	Area (Å^2)	Ref.
Smectites	*ca.* 66	*a*
$Zr(HPO_4)_2 \cdot nH_2O$	24	*c*
KNb_3O_8	17	*d*
$K_{0.85}Ti_{0.85}Nb_{1.15}O_5$	15	6
$K_4Nb_6O_{17} \cdot nH_2O$	12	8
$Na_2Ti_3O_7$	12	*h*
$Na_xMoO_3 \cdot nH_2O$		
$x = 0.5$	15	3
$x = 0.65$	11	3
$Na_xWO(P_2O_7) \cdot nH_2O$		
$x = 1.41$	13	*b*
$x = 1.00$	18	*b*
$Sn_xH_yWO(P_2O_7) \cdot nH_2O$		
$2x + y = 0.46$	39	*b*
Muscovite	23	*a*
$CsTi_2NbO_7$	18	*e*
$Cs_{0.7}Ti_{1.65}Mg_{0.35}O_4$	17	*f*
$HTiNbO_5$	12	*g*
$Tl_2Ti_6O_{13}$	12	*i*
$NaCrO_2$	8	*j*

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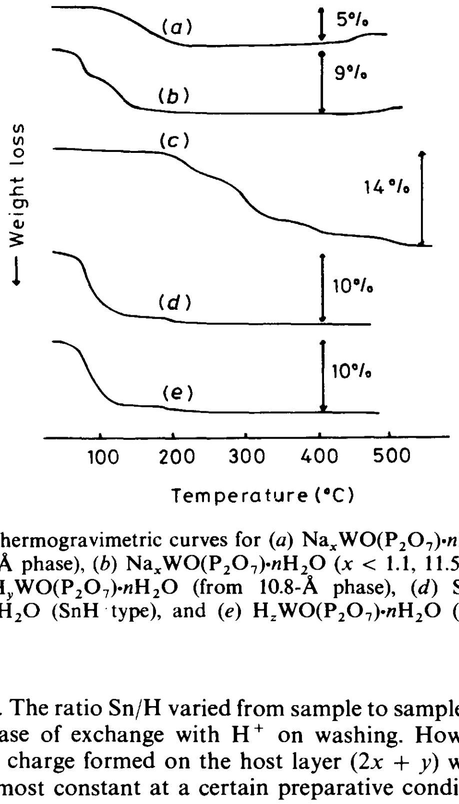

Figure. Thermogravimetric curves for (*a*) $Na_xWO(P_2O_7) \cdot nH_2O$ ($x >$ 1.1, 10.8-Å phase), (*b*) $Na_xWO(P_2O_7) \cdot nH_2O$ ($x <$ 1.1, 11.5-Å phase), (*c*) $Na_xH_yWO(P_2O_7) \cdot nH_2O$ (from 10.8-Å phase), (*d*) $Sn_xH_yWO(P_2O_7) \cdot nH_2O$ (SnH type), and (*e*) $H_zWO(P_2O_7) \cdot nH_2O$ (from SnH type)

as water. The ratio Sn/H varied from sample to sample, because of the ease of exchange with H^+ on washing. However, the negative charge formed on the host layer ($2x + y$) was found to be almost constant at a certain preparative condition. The negative charge per W generated on the host layer ranged from about 0.4 to 0.8.

As seen in Table 2, the most hydrated state of the SnH type has a basal spacing of 12.2 Å with n about 2.3. At a relative humidity of $<10\%$, a single phase with a basal spacing of 10.6 Å was observed, having n *ca.* 0.8. In addition to these basal spacings, one of 11.2 Å was observed in the course of dehydration in air. This is considered to be caused by interstratification of the 12.2- and 10.6-Å states, because the 11.2-Å state was not observed when the sample was kept at constant humidity. After dehydration, the compound disintegrated to amorphous material.

Ion Exchange with Protons and Oxidation.—Ion exchange of the SnH type product with H^+ was found to be complete, and $H_zWO(P_2O_7) \cdot nH_2O$ was formed. On the other hand, the degree of exchange of Na^+ in the sodium-type product with proton was $<100\%$: 68% of Na^+ was replaced in the case of $Na_{1.32}WO(P_2O_7) \cdot nH_2O$. The basal spacing for the most hydrated state of all the H^+ derivatives is 12.2 Å and coincides with that of the SnH type. The t.g.a. curves for H^+ derivatives in Figure (*c*) and (*e*) clearly show the difference in dehydration temperatures; the H^+ derivative from the sodium type has dehydration temperatures much higher than that from the SnH type. The last H^+ derivative shows very similar dehydration behaviour to that of the SnH type. The difference in dehydration temperature is considered to be related to the different degree of reduction of W on the host layers. The second step of weight loss for the H^+ derivative formed from the SnH type is considered to be caused by removal of protons as water.

The colour of the intercalated compounds paled upon oxidation with various oxidizing agents, but quantitative production of $[WO(P_2O_7)]$ was found to be difficult. Oxidation was very slow in the case of $KMnO_4$ solution or caused formation of different compounds in an H_2SO_4 solution of $Ce(SO_4)_2$. Upon oxidation with H_2O_2, $[WO(P_2O_7)]$ was formed, together with an amorphous material.

Discussion

Cations and water molecules enter easily into the interlayer spaces of $[WO(P_2O_7)]$ on reduction of W with strong reducing agents. The reaction is represented as in equation (1). When $Na_2S_2O_4$ is used, A^{m+} is Na^+ and $y = 0$. In an acidic solution of

$$xA^{m+} + yH^+ + (mx + y)e^- + nH_2O + [WO(P_2O_7)] \longrightarrow A^{m+}{}_xH_y[WO(P_2O_7)]^{(mx+y)-} \cdot nH_2O \quad (1)$$

$SnCl_2$, products with $A^{m+} = Sn^{2+}$ and $y > 0$ are obtained. The maximum value of ($mx + y$) was 1.41 for $Na_xWO(P_2O_7) \cdot nH_2O$ and indicates that part of W was reduced to W^{4+} and the remainder was W^{5+}. Part of W^{6+} remained upon reduction with the acidic $SnCl_2$ solution.

The compounds $A_xH_yWO(P_2O_7) \cdot nH_2O$ may be compared with layered MoO_3 bronzes. Shöllhorn *et al.*[3] prepared $Na_xMoO_3 \cdot nH_2O$ (x *ca.* 0.5) by reducing MoO_3 with $Na_2S_2O_4$ and also $Na_xH_yMoO_3 \cdot nH_2O$ ($0.65 < x + y < 1$) by cathodic reduction. The unhydrated bronze $Na_{0.5}MoO_3$ has a basal spacing expanded by 2.6 Å from that of MoO_3. This increase in basal spacing is comparable to that of 1.9 Å for the unhydrated sodium type product from [$WO(P_2O_7)$]. Reduction of $MoO_3{\cdot}2H_2O$ with acidic $SnCl_2$ solution results in insertion of hydrogen, but not of Sn^{2+}.[9]

Obviously hydrogen bonding between interlayer water and the non-planar host phosphate layer plays an important role in determining the basal spacings of layered phosphates, especially for those containing H^+. As seen in Table 1, basal spacings > 12 Å were maintained for the H^+ derivative from the SnH type product although this derivative contained less water than the most hydrated 11.5-Å phase of the sodium type. Formation of hydrogen bonds and hence an interlayer hydrated structure depends also on the number of Na^+ ions and their distribution in the interlayer spaces, because of steric hindrance. This steric hindrance may explain why different series of hydrated states are observed for the sodium type, depending on the amount of Na^+. Generally, an increase in basal spacing of about 2 Å is observed for phosphates with layered structures on changing the hydrated states.[10,11] The changes in the basal spacings and amounts of water in the interlayer spaces among the hydrated states of the 11.5-Å phase are small, especially between the 10.8- and 10.4-Å phases. The fact that this compound is rich in PO_4 groups which easily form hydrogen bonds might make a variety of hydrated states possible.

In Table 3 the areas occupied by a monovalent cation in the interlayer spaces are listed for oxides with layered structures. These areas correspond to areas per negative charge which is hypothesized to be distributed uniformly on the host layer. Almost all layered compounds have areas >10 $Å^2$. Clay minerals have extraordinarily large areas. The only exception is $NaCrO_2$ having an area of about 8 $Å^2$. In this structural type, the alkali-metal ions are well surrounded by oxygens, as is known from the fact that it can be derived from the sodium chloride structure. In $Na_xMoO_3{\cdot}nH_2O$, protons are taken up into the interlayer space as well as Na^+ when $x > 0.65$ and the area is < 11 $Å^2$.[3] The negative charge per W and on the layer of [$WO(P_2O_7)$] could be varied continuously from 1.41 for the sodium type to 0.46 for the SnH type. These negative charges correspond to areas per charge of 13 and 39 $Å^2$. The first value is close to the lower limit of 10 $Å^2$. Therefore the sodium type with x much greater than 1.41 is hardly expected to be prepared. The largest area per charge, 39 $Å^2$, is close to the values for clay minerals. Here we can control the area per charge over a wide range by regulating the degree of reduction of [$WO(P_2O_7)$].

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