by repeated precipitations from a filtered toluene solution into acetonitrile (two times) and hexanes (two times). The polymer was dried under vacuum (2×10^{-6} mmHg) for 48 h. Integration of the peaks from a ^{31}P NMR spectrum indicated that the molecular formula was $[NP(NMe_2)_{0.8}(NHB_3N_3\{NH_2\}_2Me_3)_{0.7}(NH_2)_{0.5}]_n$. Yield 0.93 g (45%). Elemental analysis calculated for $[NP(NMe_2)_{0.8}(NHB_3N_3\{NH_2\}_2Me_3)_{0.7}(NH_2)_5]_n$: C, 21.69; H, 7.67; N, 37.6; B, 11.08. Found: C, 20.21; H, 6.96; N, 24.33; B, 24.33, Cl, <2.5.

Preparation of Mixed-Substituent Poly(dimethylamino)borazinylamino)polyphosphazene) $[NP(NMe_2)_{1.4}(NHB_3N_3Me_5)_{0.6}]_n$ (20b) and Related Compounds. Compound **2** (15.0 g, 90.6 mmol) was dissolved in a mixture of THF (500 mL) and triethylamine (50 mL) using a 1000-mL three-necked flask equipped with an addition funnel and reflux condenser. After heating this solution to reflux, **16a** (1.00 g, 10.1 mmol) in THF (150 mL) was added dropwise via the addition funnel. After complete addition of the polymer solution, the reaction solution was heated to reflux for an additional 24 h, and the mixture was then allowed to cool to room temperature. The integrated peak areas from the ^{31}P NMR spectrum for the resultant polymer (**18a**, Figure 2) were consistent with the molecular formula $[NP(NMe_2)_{0.8}(NHB_3N_3Me_5)_{0.6}Cl_{0.6}]_n$. The reaction flask was equipped with a dry ice/acetone condenser. A large excess of dimethylamine (50.0 g, 1.11 mol) was condensed into the reaction flask, and the mixture was stirred with the condenser in place for 12 h. The solution was concentrated to approximately 75 mL, and the precipitated salts were removed by suction filtration through a course glass frit. Polymer **20b** was recovered by repeated precipitations from a filtered toluene solution into acetonitrile (two times) and hexanes (two times). The polymer was dried under vacuum (2×10^{-6} mmHg) for 48 h. The integrated peak areas from the ^{31}P NMR spectrum were consistent with the formula $[NP\text{-}(NMe_2)_{1.4}(NHB_3N_3Me_5)_{0.6}]_n$. Yield 1.3 g (54%).

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Rietveld Analysis of $Na_xWO_{3+x/2}\cdot yH_2O$, Which Has the Hexagonal Tungsten Bronze Structure

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Powder neutron diffraction and Rietveld analysis were used to investigate the crystal structures of hydrated and deuterated samples of $Na_xWO_{3+x/2}\cdot yH_2O$ ($x \sim 0.17, y \sim 0.23$). The compound, which crystallizes with the symmetry of space group *P6/mmm*, is related to the hexagonal tungsten bronze structure but differs from it due to the presence of sodium and oxygen along the hexagonal tunnel. Some of the oxygens appear in the structure as water molecules. The oxygen is disordered along the *z* axis in the hexagonal cavity with sodium in the hexagonal window.

Introduction

The tungsten bronzes have the general formula M_xWO_3, where M is normally a monovalent cation. The tungsten bronzes crystallize in four different structural types: perovskite, tetragonal I, hexagonal tungsten bronze, and intergrowth tungsten bronzes. The structure of the bronze obtained depends upon the size and amount of the alkali metal. The hexagonal tungsten bronze (HTB), where $0.19 \le x \le 0.33$, normally forms with the largest cations (M = K, Rb, Cs, Tl, NH_4). The tungsten bronzes have free electrons and are metallic conductors.

During the past 2 decades, there have been reports of completely oxidized compounds that appear to have the hexagonal tungsten bronze structure. These tungstates tend to have the general formula $M_xWO_{3+x/2}$. The compounds sharing this formula include $K_2W_8O_{25}$ and $K_2W_6O_{19}$.[1,2] The potassium formulas can be written as $K_{0.25}WO_{3.125}$ and $K_{0.33}WO_{3.165}$ to show their relationship to the hexagonal bronzes more easily. The compound, $BiTaW_2O_{10}$, is another oxidized version of the tungstates.[3] These compounds are of interest because the alkali-metal cation, and the additional oxygen must lie along the one-dimensional hexagonal tunnel. Attempts at solving the structures by X-ray analysis of single crystals have not succeeded in locating all the atoms.[3,4] For the potassium phases, oxygen could not be located in the hexagonal tunnel. In $BiTaW_2O_{10}$, bismuth and oxygen were forced into positions that gave an unrealistic Bi–O bond distance.[3]

The potassium tungstates are known to undergo the redox reaction

$$K_xWO_3 \leftrightarrow K_xWO_{3+x/2}$$

This reaction indicates that the oxygen atoms diffuse in and out of the hexagonal tunnel. (The 123-superconductor undergoes a similar type redox reaction.) To date, it is not yet understood how the oxygen diffuses in and out of the hexagonal tunnel. The problem is that the oxygen must

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somehow move around the potassium atom, which is in either the hexagonal cavity or the window leading into the cavity.

While studying the hydrothermal synthesis[5,6] of metal tungstates, we prepared a compound that gave an X-ray pattern similar to the hexagonal tungsten bronzes. Chemical analysis gave the composition as $Na_{0.24}WO_{3.12}\cdot 0.5H_2O$. This compound is of interest because sodium is normally too small to stabilize the hexagonal framework. Not only is oxygen inside the hexagonal tunnel, but the composition indicates that water molecules must also reside in the structure. The facts that sodium can be exchanged for hydrogen and that after dehydration the compound reabsorbs most of its water[6] indicate that the atoms can easily diffuse out of the one-dimensional hexagonal tunnel very much like the oxygen in the potassium polytungstates. To elucidate the location of all atoms, we used Rietveld analysis of powder neutron diffraction data taken on both a hydrated and a deuterated sample of the compound. Neutron diffraction has a great advantage over X-ray diffraction in cases where the characterization of low atomic number atoms such as oxygen and sodium is of interest in a compound that contains atoms of much higher atomic member such as tungsten. It was our hope that pinpointing the location of the atoms would aid in understanding the redox and ion-exchange reactions that these compounds are known to undergo.

Experimental Section

The hydrated and deuterated samples were prepared in the following manner: 20 mL of a 1 M $Na_2WO_4\cdot 2H_2O$ solution was acidified to pH 1.5 with the appropriated amount of 1 N HCl. The solution was heated to 155 °C for 3 days in a Parr acid digestor. The resulting white product was filtered and dried with ethanol. For the deuterated sample, $Na_2WO_4\cdot 2H_2O$ was heated to 150 °C to drive off the water of hydration. 20% DCl in D_2O and pure D_2O obtained from Aldrich Chemical were used instead of H_2O and HCl. A 1 M DCl solution was prepared by diluting the concentrated DCl solution with the appropriate amount of D_2O. The deuterated sample was then prepared under the same conditions as the hydrated compound. The product was filtered and washed with D_2O. The compounds were then immersed in D_2O until sent for neutron diffraction to limit the $D^+ \leftrightarrow H^+$ exchange reaction. The samples were checked by X-ray powder diffraction, and all peaks could be indexed on the hexagonal tungsten bronze structure.

The neutron diffraction measurements were made at room temperature with the high-resolution five-counter neutron diffractometer at the National Institute of Standards and Technology. Approximately 10 g of sample were placed in a 10-mm vanadium diameter can. Data was collected from 10° to 115° in steps of 0.05° with $\lambda = 1.553$ Å. The structure was refined using the Rietveld method[7] adapted to the five-counter diffractometer and modified to include background parameters.[8] The neutron scattering amplitudes of the atoms were $b(W) = 0.477$, $b(O) = 0.5805$, $b(Na) = 0.363$, $b(D) = 0.6674$, and $b(H) = -0.374$. Detector 5 was excluded from the refinement due to the lack of peaks above 95°. During the analysis, background parameters, scale factor, cell dimensions, half-width parameters, and structural parameters were refined.

Structure Analysis

Precise hexagonal unit cell dimensions of the samples were obtained by least-squares fit of the peak positions in the X-ray powder diffraction pattern. There was no evidence in the X-ray powder pattern for the doubling of the c axis as is observed in the tungsten bronzes.[9] The space group chosen for the refinement was $P6/mmm$, as in the compound $Pb_xM(OF)_{3+x/2}$ where M = Ta, Nb.[10] This compound has the hexagonal tungsten bronze structure and is similar to our compound with both a cation and an anion along the hexagonal tunnel.

The structural analysis was started using data collected from the hydrated compound. Tungsten atoms were placed in the 3f site at (0.5,0,0), O2 in 6l at $(x,2x,0)$ where $x = 0.21$, and O1 in 3g at (0.5,0,0.5). The structure refined to $R_B = 35\%$ and $R_{wp} = 9\%$. At this point, sodium was placed at 1b (0,0,0.5) and O3 at 1a (0,0,0). The occupancies did not refine near the chemical composition. Attempts at disordering sodium or oxygen along $(0,0,z)$ proved fruitless, because the atoms refined back to their original positions. Sodium and oxygen at these positions gave an unrealistic Na–O bond distance of 1.9 Å. Switching the sodium and oxygen atoms did not improve the refinement. The best R values obtained were $R_B = 17\%$ and $R_{wp} = 7.2\%$.

The deuterated sample was prepared in the hope of improving the refinement and of locating the water molecules. There was a slight improvement in the background compared to the hydrated sample but the height of the background suggests that there was probably some isotopic $D^+ \leftrightarrow H^+$ exchange. We believe that the exchange occurred with the surface water. No evidence for doubling the c axis was apparent in the neutron pattern, and the refinement was started with the space group $P6/mmm$. The WO_3 framework positions were as described before. Initial refinement included only the framework atoms. Examination of the profile fit at this stage showed that all the peaks in the spectra were accounted for and that the space group chosen was reasonable. A difference Fourier map indicated there were atoms at (0,0,0) and (0,0,0.5). Sodium was placed at (0,0,0) and oxygen at (0,0,0.5), which is at the center of the hexagonal cavity. The R values fell to $R_B = 27\%$ and $R_{wp} = 7.4\%$. Difference Fourier indicated scattering along $(0,0,z)$ with $z \sim 0.35$ and at $(x,2x,z)$ with $x \sim 0.07$ and $z \sim 0.3$. The scattering along $(0,0,z)$ indicated that O3 was disordered along the z axis. Refinement of the z position led to lower R values and $z = 0.401$. The atom at $(x,2x,z)$ was approximately 1 Å away from O3, which indicated that the atom was deuterium. Placing deuterium at this position led to a refinement of the position approximately 1.0 Å away from O3 and to a reasonable occupancy. The R values dropped to $R_B = 17\%$ and $R_{wp} = 7\%$. The isotropic temperature factors of WO_3 were refined which lowered R_B to 12%. At this point, a plot of the profile showed the Gaussian shape was inadequate to describe the peak shape. The Rietveld program uses a Pearson type VII function, which allows the line shape to be changed continuously from Gaussian to Lorentzian through the addition of one additional parameter. The best refinement was with $2m = 10$. Table I gives all the final refinement values.

After location of deuterium, the data from the hydrated sample were reexamined. A difference Fourier map indicated large negative scattering at $(x,2x,z)$ in the same vicinity as deuterium. Since hydrogen has a negative scattering amplitude for neutrons, it seemed reasonable to place hydrogen at this position. The refinement improved remarkably, with reasonable occupancies for the sodium and oxygen occupancies. The R values dropped

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Table I. Positional Parameters for $Na_xWO_{3+x/2}{\bullet}yD_2O$[a]

atom	site	x	y	z	B	occup
W	3f	0.5	0	0	3.8 (4)	3.0
O1	3g	0.5	0	0.5	1.5 (1)	3.0
O2	6l	0.2114 (4)	$2x$	0.0	1.2 (1)	6.0
O3	2e	0	0	0.412 (4)	2.6 (8)	0.99 (2)
D	12o	0.071 (3)	$2x$	0.312 (7)	1.0	1.14 (3)
Na	1a	0	0	0	1.0	0.51 (2)

$a = 7.329$ (2) Å $c = 3.891$ (1) Å

$R_B = 9.02\%$ $R_P = 5.06\%$ $R_{wp} = 6.38\%$ $R_E = 5.81\%$

GoF = 1.10

$$R_B = \frac{\sum|I(\text{obs}) - I(\text{calc})|}{\sum I(\text{obs})}$$

$$R_P = \frac{\sum|y(\text{obs}) - y(\text{calc})|}{\sum y(\text{obs})}$$

$$R_{wp} = \left|\frac{\sum w[y(\text{obs}) - y(\text{calc})]^2}{\sum w[y(\text{obs})]^2}\right|^{1/2}$$

$$R_E = \left|\frac{N - P + C}{\sum w[y(\text{obs})]^2}\right|^{1/2}$$

[a] N = number of independent observations, P = number of parameters, C = number of constraints, y = counts at angle 2θ, I = integrated Bragg intensities, and w = weights.

Table II. Positional Parameters for $Na_xWO_{3+x/2}{\bullet}yH_2O$

atom	site	x	y	z	B	occup
W	3f	0.5	0	0	3.9 (3)	3.0
O1	3g	0.5	0	0.5	1.5 (1)	3.0
O2	6l	0.2120 (3)	$2x$	0.0	1.9 (2)	6.0
O3	2e	0	0	0.415 (6)	1.2 (4)	0.81 (2)
H	12o	0.065 (4)	$2x$	0.302 (6)	1.0	1.20 (3)
Na	1a	0	0	0	1.0	0.51 (4)

$a = 7.331$ (1) $c = 3.891$ (6)

$R_B = 9.72\%$ $R_P = 5.40\%$ $R_{wp} = 6.83\%$ $R_E = 6.20\%$

GoF = 1.12

to acceptable values. Table II shows the positions of the atoms along with the final R values. The peak shape of the hydrated sample was adequately described by a Gaussian distribution.

Discussion

The structure of the hexagonal tungsten bronze was originally worked out by Magneli.[9] Like all tungsten bronzes, the hexagonal structure possesses a rigid tungsten–oxygen framework built up of layers containing corner-shared WO_6 octahedra that are arranged in six-membered rings. The layers are stacked along the [00l] axis, giving rise to one-dimensional tunnels, Figure 1. Doubling of the c axis arises because the tungsten atoms are slightly displaced in the xy plane with respect to tungsten atoms in the plane above and below. Magneli placed the metal cation in the center of the hexagonal tunnel and solved the structure in the space group $P6/mcm$.

The main features of this structure have never been questioned, but Dickens,[11] using powder neutron diffraction, which is more sensitive to oxygen location, and modern single-crystal X-ray techniques found some discrepancy in Magneli's structure. The most significant new feature is the puckering of the ring of six oxygens forming the hexagonal window. This distortion of the WO_6 octahedra removes the glide plane and inserts a screw axis, which changes the space group to $P6_3/22$. Dickens also found that the potassium atom was disordered along {0,0,z} near the center of the hexagonal cavity.

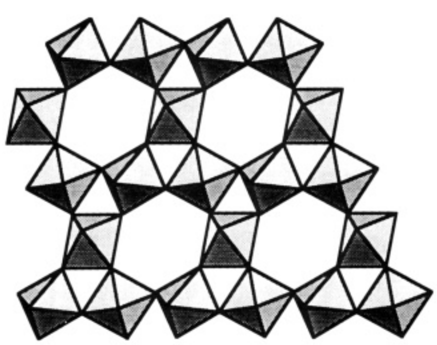

Figure 1. HTB structure, showing the WO_6 octahedra arranged to form hexagonal tunnels, viewed along [001] axis.

Although the general structure of the compound synthesized here is close to that of HTB, there are several important differences. First, the sodium atoms are not located in the hexagonal cavity of anions between the layers of the transition-metal atoms. Instead, the sodium atoms are in the transition-metal plane, in the hexagonal window surrounded by a ring of six oxygens. Second, the tungsten atoms are located at (0.5,0,0) and are not displaced along the x axis as in the hexagonal bronzes, so there is no doubling of the c axis. There is no evidence for the puckering of the WO_6 octahedra that is found in K_xWO_3. The WO_6 octahedra are perfectly symmetrical with the oxygen atoms in the same plane as the tungsten atom.

The most important difference is the deviation of the compound from the normal tungsten bronze stoichiometry of M_xWO_3 which arises from the presence of oxygen in the hexagonal cavity. Unlike the tungsten bronzes, which are reduced compounds, the phases synthesized here are completely oxidized with the formal oxidation state of tungsten being its highest valence.

After the location of all the atoms, structural refinement in space group $P6/mmm$ was fairly straightforward. The profiles of the deuterated and hydrated phases are shown in Figure 2 and 3. The structural parameters of both phases are listed in Tables I and II. The quality of the refinement is shown by the goodness of fit parameter (GoF) which is simply the ratio of R_{wp}/R_e. The GoF is 1.12 for the hydrated sample and 1.10 for the deuterated sample. R_{wp}/R_e tends to be misleadingly low if the background is high. In fact, there are cases of ratios less than 1.25 when the model includes only background, no crystal structure at all. A value of 1.0 indicates that the deviations can be explained by purely random fluctuations and that there is therefore no more information to be extracted from the data.

The composition derived from the refinements are $Na_{0.17}WO_{3.085}{\cdot}0.23D_2O$ and $Na_{0.17}WO_{3.085}{\cdot}0.19H_2O$ for the deuterated and hydrated samples, respectively. As can be seen, the compositions obtained from the refinement are very similar. The refined water contents are slightly different, but are within the range of statistical uncertainty. The water content obtained from the refinement is approximately half the value determined from the chemical composition. The remaining water is believed to be water adsorbed on the surface. A similar discrepancy was noted for $WO_3{\cdot}{}^1/{}_3H_2O$ and also attributed to adsorbed water.[12]

The most important result of the refinement was the location of the oxygen atoms in the hexagonal tunnel. As

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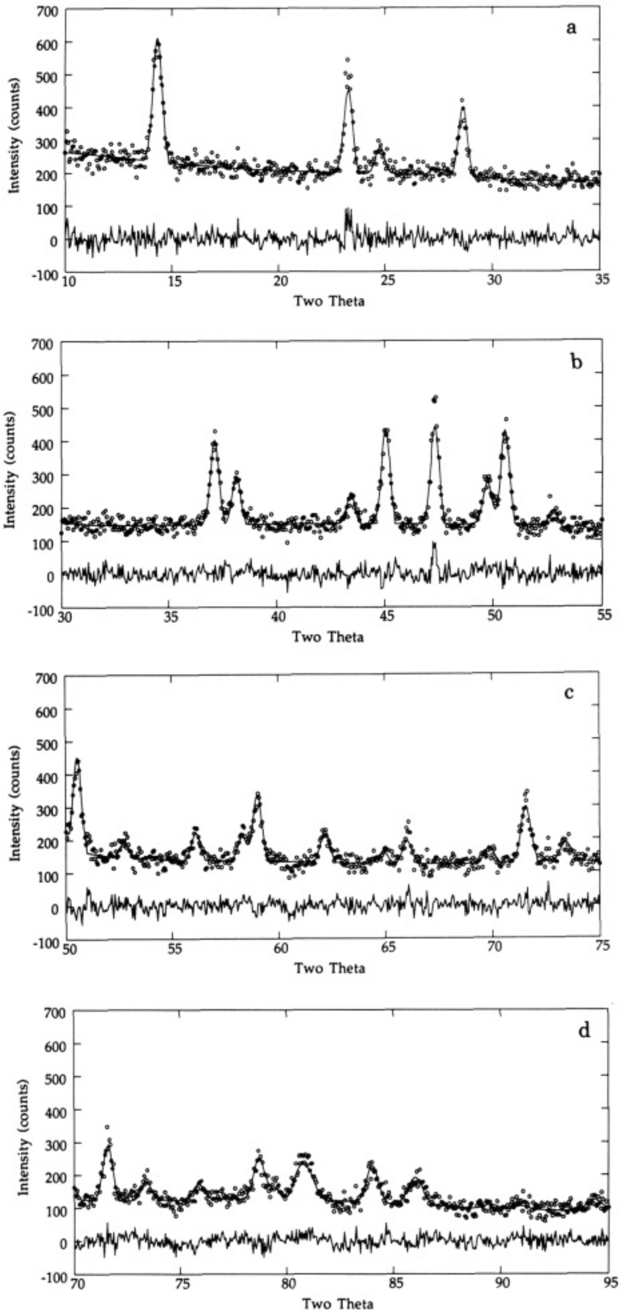

Figure 2. Observed, calculated, and difference profiles of $Na_xWO_{3+x/2}{\cdot}yH_2O$.

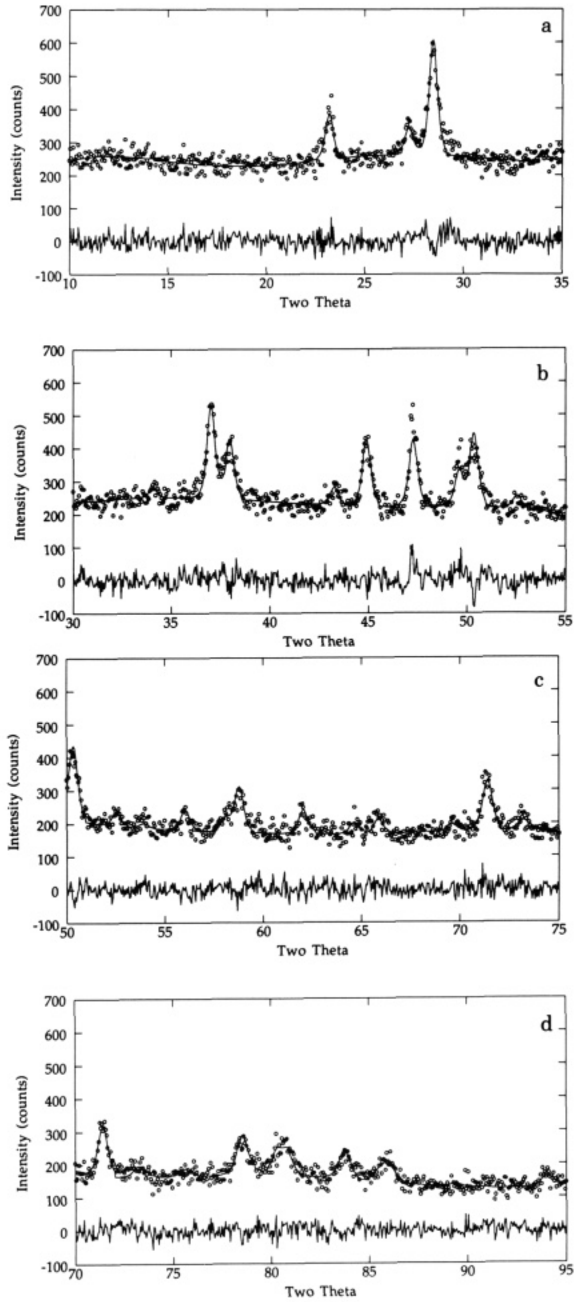

Figure 3. Observed, calculated, and difference profiles of $Na_xWO_{3+x/2}{\cdot}yD_2O$.

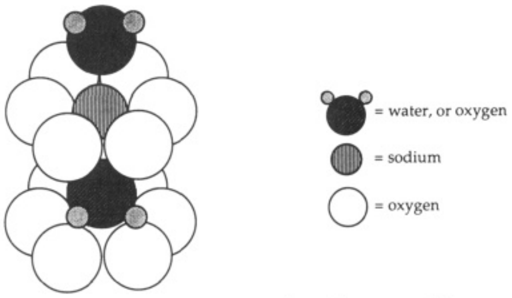

Figure 4. Atom positions in tunnels of hexagonal bronze. The structure of $Na_xWO_{3+x/2}{\cdot}yH_2O$ with sodium in the hexagonal window surrounded by six oxygen atoms and the water molecules in the hexagonal cavity. Not drawn to scale.

seen from Tables I and II, the refinement showed that the oxygen atoms were located in the hexagonal cavity and disordered along the *z* axis. The sodium atoms are located at the center of the hexagonal window. These results are shown in Figure 4. Any attempts to disorder sodium along any plane gave undesirable errors in the positional parameters. Examination of atomic radii tells us that the Na–O bond distance should be approximately 2.35 Å. If oxygen is at the center of the hexagonal cavity (0,0,0.5), the Na–O bond distance would be 1.9 Å, which is too short. The bond distance can be increased by disordering O3 along the *z* axis which occurs to give a Na–O bond distance of 2.27 (2) Å. From consideration of atomic radii this bond distance is 0.08 Å shorter than expected, but bond lengths of this order have been seen in other compounds.[13] The other Na–O bond length which results from the disordering is 1.6 Å, which is clearly much too short. This can be discarded only if all the oxygen atoms are placed in the atomic position farthest from the sodium site and some sodium sites are not occupied. The sodium content of 0.17

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Table III. Important Bond Distances (Å) and Angles (deg)

	hydrated	deuterated
W–O1	1.889 (1)	1.896 (1)
W–O2	1.945 (1)	1.945 (1)
Na–O3	2.27 (3)	2.27 (2)
O–H	0.91 (3)	0.95 (4)
Na–O1	2.678 (5)	2.683 (6)
O3–O2	3.670 (6)	3.678 (3)
O3–O1	3.13 (4)	3.14 (4)
O2–O1	2.713 (10)	2.717 (1)
O1–O1	2.679 (5)	2.686 (5)
H–O–H	108 (2)	114 (3)

Na/W determined from the refinement is important for maintaining a reasonable Na–O bond distance because the refined value is half the occupancy for the site, resulting in every other sodium site being empty. If more of the sites are filled, then the Na–O distance of 1.6 Å cannot be ignored.

Attempts at refining the structure with sodium in the center of the hexagonal cavity and oxygen in the window gave significantly higher *R* values. From electrostatic considerations, sodium in the hexagonal window surrounded by six oxygens is more desirable then having the negatively charged oxygen in this position. In $Pb_xM(O,F)_{3+x/2}$, the lead cation was found in the hexagonal window with oxygen in the cavity. In this structure, lead is disordered along $(x,2x,z)$ with z approximately zero to increase the Pb–O bond distance.[10] For the compound $FeF_3\cdot{}^1/_3H_2O$, which is related to the HTB phase, water molecules reside in the centers of hexagonal cavities and not in the rings of anions forming the hexagonal window.[14] The water molecules are not disordered in the structure.

Table III gives the most important bond distances and angles in the structure. The O–D and O–H bond lengths are 0.95 and 0.91 Å. These values are well within the range found for water molecules. The D–O–D bond angle at 114° is greater then the H–O–H at 108°. The water bond angle for the hydrated phase is fairly typical of water molecules. The D–O–D bond angle is at the upper end of the bond angles found for water molecules.[15,16] The differences in the bond angles result from the different atomic positions of deuterium and hydrogen in the structure, but the difference probably is not significant. A similar D–O–D bond angle was found in the defect pyrochlore $Na_{1.0}W_2O_{6.55}\cdot D_2O$.[17] The W–O1 and W–O2 bond distances of 1.889 and 1.945 Å for the deuterium sample and 1.896 and 1.945 Å for the hydrated sample are well within the range of 1.85–2.0 Å for the WO_6 octahedra found in the hexagonal bronzes.[9]

Not every oxygen in each layer is a water molecule. To balance the charge of sodium, approximately 0.09 oxygen ions must be present. It is possible that a combination of hydroxyl and oxygen ions balance the charge of the sodium atoms, but we were not able to differentiate between the two different ions. This can be accomplished by having about two-thirds of the oxygen atoms in the structure being in water molecules. It might be expected that this would lead to some type of ordering of atoms in the structure and a need to increase the *c* axis to account for the new symmetry, but this is not seen. Superstructures have been reported for the compound $K_{0.33}WO_{3.165}$. In the original synthesis,[3] the *c* lattice parameter was made approximately 29 Å in order to index small peaks in the pattern that were believed to indicate an ordering of atoms in the structure, but no evidence for a doubled (or higher) *c* axis was found, in this study, in either the neutron or X-ray powder pattern. This lack of doubling suggests that the ordering is probably on the local level and not long distance, which is consistent with a high mobility of the species in the tunnels.

The temperature factors for W, O1, and O2 were refined, and the values for oxygen are typical of oxygen atoms in a rigid framework. The thermal parameter of tungsten is quite high, perhaps because the tungsten atoms do not sit exactly on the 3f site. Another explanation is that the thermal parameters tend to correlate with the background and the tungsten parameter might be affected by the high background. Large thermal parameters of heavy atoms are not uncommon in Rietveld refinements of powder data. The thermal parameter of the water oxygen is typical of mobile ions. The thermal parameters of the remaining atoms were fixed at 1.0 $Å^2$ after refinement led to extremely high values.

The mechanism for the diffusion of the species out of the hexagonal tunnel is not clear since sodium is in the hexagonal window and may block any movement along the *z* axis. One possible mechanism is for the sodium to be displaced into the large cavity, allowing the water molecules to pass by. Alternatively, oxygen motion could possibly be via exchange with the lattice oxygen; elucidation of the diffusion mechanism will require isotopic studies. The diffusion of sodium out of the structure during ion exchange is easier to understand. To leave the structure, sodium must move into the hexagonal cavity, where there is ample room for the sodium ion to move around the oxygen.

For the redox reaction of the potassium polytungstates, discussed in the Introduction, it has been proposed that the oxidation–reduction reaction is a simple diffusion of oxygen ions out of the lattice.[18] Others have argued that since the temperature for the redox reaction is between 500 and 600 °C and the reduction takes 24–48 h, the reaction is not a simple continuous transformation but a complicated mechanism involving the nucleation and growth of a new phase.[3] However, the growth and nucleation mechanism can probably be ruled out for the dehydration reaction

$$Na_{0.17}WO_{3.085}\cdot 0.22H_2O \leftrightarrow Na_{0.17}WO_{3.085}$$

because the temperature, <250 °C, at which it occurs is too low. The ion exchange of sodium for hydrogen at 80 °C also shows the high mobility of ions in this structure at temperatures well below where nucleation of a new phase is likely. As oxygen must leave the structure in both the dehydration and reduction reactions, it is probable that the mechanism for the oxidation–reduction reaction of the potassium compound is also a simple diffusion of the oxygen ions out of the structure.

Conclusion

The location of the atoms in the hexagonal bronze like phase of $Na_xWO_{3+x/2}\cdot yH_2O$ has been found by the Rietveld analysis of powder neutron diffraction data. The position of the oxygen has been found in the hexagonal cavity, where the alkali atoms normally reside in the hexagonal tungsten bronzes. The hexagonal window is occupied by a sodium atom. The oxygen is disordered along the *z* axis

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to increase the Na–O bond distance.

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Registry No. $Na_{0.17}WO_{3.085}\cdot 0.19H_2O$, 138540-49-5; $Na_{0.17}WO_{3.085}\cdot 0.23D_2O$, 138540-48-4.

Photoelectron Transfer Mediated by Size-Quantized CdS Particles in Polymer-Blend Membranes

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Size-quantized cadmium sulfide (CdS) particles have been in situ generated in 300–400-Å-thick polymer-blend membranes (PBMs) prepared from mixtures of poly(styrenephosphonate diethyl ester) (PSP) and cellulose acetate (CA). Absorption spectroscopy of CdS particles in PBMs prepared from PSP:CA = 1:4, 1:1, 2:1, and 4:1 indicated bandgaps of 2.81, 2.63, 2.58, and 2.48 eV and, hence, size quantization. Mean diameters of CdS particles in PBMs prepared from PSP:CA = 1:4, 1:1, and 4:1 have been assessed from transmission microscopy to be 44, 58, and 82 Å. Excitation of CdS particles in PBMs at 400 nm resulted in observable emission spectra with maxima at 490 and 570 nm (PSP:CA = 1:4), 514 nm (PSP:CA = 1:1), 548 nm (PSP:CA = 2:1), and 580 nm (PSP:CA = 4:1). Emission of CdS particles embedded in PBMs was found to be quenched by methylviologen (MV^{2+}). Also, bandgap illumination resulted in photoelectron transfer to produce $MV^{\bullet +}$. More efficient photoelectron transfer was observed for smaller CdS particles than for larger ones.

Introduction

Preparation, characterization, and utilization of size-quantized semiconductor particles continue to be the subject of vigorous research activity.[3-9] Confinement of the electron and hole in a particle that is smaller than the exciton diameter in the bulk semiconductor (i.e., size quantization) often results in beneficial mechanical, chemical, electrical, and electrooptical properties.[10] Preparation and stabilization of nanosized semiconductor particles require, however, carefully controlled experimental conditions and/or the presence of a supporting matrix. In our laboratories, we have prepared and characterized size-quantized semiconductor particles in surfactant vesicles,[11] at the interfaces of monolayers[12-17] and bilayer lipid membranes,[18-20] and between the polar headgroups of Langmuir–Blodgett films.[21] Preparations at monolayers interfaces have been shown to be particularly useful since this method allowed a convenient morphology and dimensionality control and the transfer of the incipient semiconductor particles to slid support at different stages of their growth. In principle, a similar degree of control can be accomplished in ultrathin functionalized polymeric films.

Encouraged by the reported use of polymer films as matrices for semiconductor particles,[22-27] we have recently launched investigations into the formation of semiconductors in polymer-blend membranes (PBMs) prepared

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