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# Syntheses of Hydrated Molybdenum Bronzes by Reduction of $MoO_3$ with $NaBH_4$

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Hydrated molybdenum bronzes have been prepared by reduction reaction of $MoO_3$ with $NaBH_4$ in ethanol and DMSO. The reduction reactions in both solvents occur smoothly; thus, the layered structure of $MoO_3$ is maintained in the product. Divalent cation $Ca^{2+}$ has been intercalated between the $MoO_3$ layers, which leads to highly reduced molybdenum bronze ($Mo^{5.26+}$). Solvated molybdenum bronze catalyzes the reduction reaction of DMSO by $NaBH_4$, producing $CH_3SCH_3$. The structure model of hydrated sodium molybdenum bronze has also been reinvestigated by using the Rietveld analysis. The hydrated molybdenum bronze crystallizes in an orthorhombic structure, in which the structure of Mo octahedron layers is closely related to that in $MoO_3$. However, the structure refinement reveals that the Mo octahedron in the $MoO_3$ layers is axially distorted, which is different from that in $MoO_3$ but similar to an isoelectron compound $H_{0.33}MoO_3$.

## Introduction

$MoO_3$ adopts a layered structure that consists of two-dimensional layers built up with corner- and edge-shared $MoO_6$ octahedra. Different guest molecules or cations, such as alkali metal ions[1−9] and organic molecules,[10−13] have been intercalated between the $MoO_3$ layers. The intercalated compounds, or molybdenum bronzes, are of interest because of their low dimensional physical properties and the potential applications in battery and electrochromic devices. Conventional syntheses of the hydrated alkali metal molybdenum bronzes involve suspension of $MoO_3$ in a neutral aqueous solution in the presence of reducing reagent.[2,3] The $MoO_3$ layers take up electrons from the reducing reagent and become negatively charged. Simultaneously, an equivalent amount of cations, often the hydrated cations, is intercalated into the interlayer space. Up to now only $Na_2S_2O_4$ has been known to be a suitable reducing reagent for $MoO_3$. The typical synthesis reaction for the hydrated molybdenum bronze can be expressed as

$$x\mathrm{Na_2S_2O_4} + (2n)\mathrm{H_2O} + 2[\mathrm{MoO_3}] \rightarrow 2\mathrm{Na}_x(\mathrm{H_2O})_n[\mathrm{MoO_3}] + (2x)\mathrm{SO_2}\uparrow \quad (1)$$

This is a topochemical reaction; hence, the framework of $MoO_3$ is retained in the product. However, the reduction reaction in aqueous solution is often accompanied by proton intercalation, and a large amount of $Na_2MoO_4$ has to be used as buffer[2,3] to maintain a suitable pH during the reaction.

Recently Tsang et al.[14−17] reported reduction of oxo ions $MO_4^{2-}$ (M = Mo, W, etc.) with $NaBH_4$ in aqueous solution. This reaction yields, however, amorphous products. The crystalline molybdenum bronzes, such as $Na_xMoO_3$ and $K_xMoO_3$, were obtained by heating the amorphous samples at about 350−500 °C.

Hydrated molybdenum bronzes crystallizes in a layered structure that is topologically related to $MoO_3$; therefore, the reduction should be applied directly on $MoO_3$. The analogous reaction of $Na_2S_2O_4$ cannot be used for $NaBH_4$ because of the different chemical behavior in aqueous solution. $MoO_3$ is a weak acid and may convert to the oxo ions $MoO_4^{2-}$ in basic solution, as shown in

$$\mathrm{MoO_3} + \mathrm{H_2O} \rightarrow 2\mathrm{H^+} + \mathrm{MoO_4}^{2-} \quad (2)$$

On the other hand, the decomposition reaction of $NaBH_4$ is catalyzed by protons in acidic solution:

$$\mathrm{BH_4}^- + 2\mathrm{H_2O} \rightarrow \mathrm{BO_2}^- + 4\mathrm{H_2} \quad (3)$$

To accomplish and simplify the synthesis reaction for molybdenum bronzes, we carried out a systematic study of the reduction of $MoO_3$ with $NaBH_4$ in organic solvents and found that the hydrated molybdenum bronze could be prepared conveniently in some organic solvents.

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(1) Schöllhorn, R.; Kuhlmann, R.; Besenhard, J. O. *Mater. Res. Bull.* **1976**, *11*, 83.

(2) Thomas, D. M.; McCarron, E. M. *Mater. Res. Bull.* **1986**, *21*, 945.

(3) Sotani, N.; Eda, K.; Kunitomo, M. *J. Solid State Chem.* **1990**, *89*, 123.

(4) Sotani, N.; Suzuki, T.; Eda, K.; Yanagi-ishi, M.; Takagi, S.; Hatayamae, F. *J. Solid State Chem.* **1997**, *132*, 330.

(5) Sotani, N.; Miyazaki, T.; Eda, K.; Hatayama, F. *J. Mater. Chem.* **1997**, *7*, 2253.

(6) Eda, K.; Miyazaki, T.; Hatayama, F.; Nakagawa, M.; Sotani, N. *J. Solid State Chem.* **1998**, *137*, 12.

(7) Eda, K.; Suzuki, M.; Hatayama, F.; Sotani, N. *J. Mater. Chem.* **1997**, *7*, 821.

(8) Greenblatt, M. *Chem. Rev.* **1988**, *88*, 31.

(9) Canadell, E.; Whangbo, M.-H. *Chem. Rev.* **1991**, *91*, 965.

(10) Chatakondu, K.; Green, M. L. H.; Qin, J. G.; Thompson, M. E.; Wiseman, P. J. *Chem. Commun*. **1988**, 223.

(11) Tagaya, H.; Ara, K.; Kadokawa, J.-I.; Karasu, M.; Chiba, K. *J. Mater. Chem.* **1994**, *4*, 551.

(12) Xu, Y.; An, L.-H.; Koh, L.-L. *Chem. Mater*. **1996**, *8*, 814.

(13) Zapf, P. J.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1997**, *9*, 2019.

(14) Tsang, C.; Dananjay, A.; Kim, J.; Manthiram, A. *Inorg. Chem.* **1996**, *35*, 504.

(15) Tsang, C.; Manthiram, A. *Inorg. Chem.* **1997**, *36*, 2206.

(16) Tsang, C.; Manthiram, A. *J. Mater. Chem.* **1997**, *7*, 1003.

(17) Tsang, C.; Kim, J.; Manthiram, A. *J. Mater. Chem.* **1998**, *8*, 425.

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In addition, Thomas et al.[2] proposed an orthorhombic structure model for the hydrated molybdenum bronzes on the basis of the structure of $MoO_3$. Although the structure of $MoO_3$ layer in their model was not suitably justified, much experimental evidence[1−7] supports their suggestion that the alkali ions are located in an octahedral or cubic site, depending on the ionic size. In this paper, we report the reduction reaction of $MoO_3$ with $NaBH_4$ in ethanol and dimethyl sulfoxide (DMSO) and the reinvestigation of the crystal structure of the hydrated molybdenum bronze using the Rietveld refinement.

## Experimental Section

**Syntheses of Molybdenum Bronzes**. $MoO_3$ powder was obtained by heating $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at 600 °C for 12 h in air. The hydrated molybdenum bronzes were prepared by reduction of $MoO_3$ with $NaBH_4$ in ethanol (EtOH) and dimethyl sulfoxide (DMSO), respectively. Ethanol (99.5%) and DMSO (A.R.) were used as received. For the reduction in ethanol, an amount of 2 g of $MoO_3$ was added to $NaBH_4$/EtOH solution that contains 0.26 g of $NaBH_4$ in 200 mL of EtOH. The suspension was standing for 36 h with vigorous stirring under $N_2$. The dark-blue product was then collected by centrifugalization and washed with EtOH until the solution was colorless. The reduction in DMSO was carried out in a similar way. Amounts of 0.39 g of $NaBH_4$ and 2.3 g of $CaCl_2$ were dissolved in 100 mL of DMSO, and 1.0 g of $MoO_3$ was added to the solution. The suspended solution was allowed to stand for 7 days under $N_2$, while the color of the suspension gradually changed from white to green and then to dark-blue. The dark-blue product was collected and washed with acetone. The ion-exchange experiment was carried out as follows. A total of 1.0 g of hydrated molybdenum bronze was suspended in 50 mL of 1 M KCl or $CaCl_2$ aqueous solution, and the suspension was stirred for 24 h. During the experiment, nitrogen gas was bubbled to prevent oxidation. The gases released from the reactions were collected and characterized by using MS, NMR, and IR techniques.

X-ray powder diffraction was carried out on a Rigaku D/max-2000 powder diffractometer with Cu Kα radiation. The diffraction pattern was indexed using TREOR90 in the Powder-X program package.[18] The structure of the hydrated molybdenum bronze was refined using the Rietveld technique with the GSAS program.[19] The analysis of the metal components (Na, Mo, and Ca) was carried out with ICP method, and the C and H contents were measured by a Vario EL element analyzer. The amounts of DMSO and $H_2O$ in the products were determined by a TGA method with a Dupont 951 TGA−DTA analyzer. IR spectra were obtained using a Nicolet Magna-IR750 spectrometer. The gas released was characterized by GC−MS (MAT-GCQ) and NMR spectroscopy.

## Results and Discussion

**Reduction Reaction in Ethanol.** Figure 1a shows the X-ray diffraction pattern of the product obtained by reduction of $MoO_3$ with $NaBH_4$ in EtOH. The diffraction pattern of a sample prepared using the $Na_2S_2O_4$ method[2] is also included in the figure (Figure 1b) for comparison. The diffraction patterns clearly show that both products are identical; thus, the product obtained by reduction of $NaBH_4$ in EtOH is indeed a hydrated molybdenum bronze. In comparison with $MoO_3$, the lattice parameter along *a* and *c* axes remains almost unchanged (Table 1), while the *b* axis, which is perpendicular to the $MoO_3$ layers, increases from 13.9 Å in $MoO_3$ to about 19.2 Å in the hydrated molybdenum bronzes. The $H_2O$ molecules in the hydrated molybdenum bronzes originate from the trace water in ethanol. A parallel reaction carried out in anhydrous ethanol yielded amorphous product; thus, a trace of water is necessary to maintain the layered structure of the products.

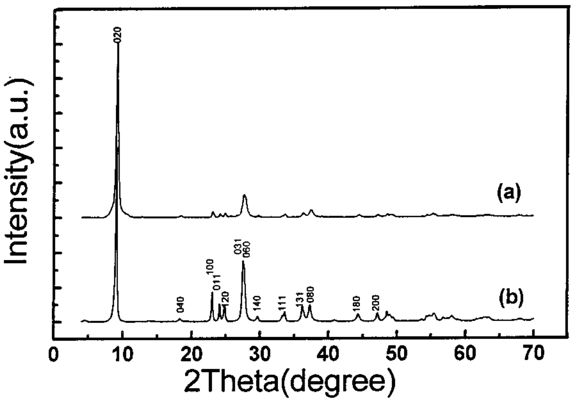

**Figure 1.** X-ray diffraction patterns of the molybdenum bronzes obtained by the reduction of $MoO_3$ with $NaBH_4$ in EtOH (a) and by the Thomas method (b).[2]

During the reaction, considerable $H_2$ was released from the system. Therefore, the reaction that occurred in the ethanol solution is proposed as

$$2[MoO_3] + (2x)NaBH_4 \xrightarrow{EtOH} 2Na_x[MoO_3] + xB_2H_6 + xH_2 \quad (4)$$

$$B_2H_6 + C_2H_5OH \rightarrow C_2H_5OH\cdot BH_3 \rightarrow C_2H_5OBH_2 + H_2 \quad (5)$$

$MoO_3$ layers took up electrons from $NaBH_4$ and simultaneously the cations, being the hydrated $Na^+$ ions in this case, intercalated between the layers, forming the hydrated molybdenum bronzes. Because boron has a high affinity for oxygen, the diborane formed in the reaction further reacted with ethanol,[20] forming $C_2H_5OBH_2$ that remained in the solution. The reaction process of $MoO_3$ with $NaBH_4$ in ethanol is rather similar to that of the transition metal ions in organic solvents.[21]

$NaBH_4$ is a strong reducing reagent; therefore, more reduced hydrated molybdenum bronzes should be obtained. Attempts to prolong reaction time yielded, however, the complex product, showing that the structure framework of $MoO_3$ was destroyed during the reaction. Regarding the cation sites available between the $MoO_3$ layers, the maximum Na/Mo ratio is 0.5 if all of the octahedral sites are occupied. Since the intercalated cations are coordinated by water molecules, the actual Na/Mo ratio should be smaller than 0.5 (about 0.3 in most of the products) in the hydrated molybdenum bronzes. A way of increasing the reduction content is to use divalent cations, such as $Ca^{2+}$, as the intercalated species. EtOH cannot be used as a solvent for such systems because of the low solubility for $CaCl_2$; therefore, we studied the reduction reaction of $MoO_3$ in dimethyl sulfoxide (DMSO).

**Reduction Reaction in DMSO.** Figure 2 shows X-ray diffraction patterns of the products obtained in DMSO. The difference in the products obtained in ethanol is the significantly large *d* spacing perpendicular to the $MoO_3$ layers (17.9 Å). The $MoO_3$ layered structure was retained so that the diffraction pattern of the product can be indexed with an orthorhombic cell of $a = 3.74$ Å, $b = 35.80$ Å, and $c = 3.85$ Å as shown in Table 1. The large *d* value along the *b* axis implies that DMSO was intercalated between the layers and that the large solvated

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(18) Cheng, D. *J. Appl. Crystallogr.* **1999**, *32*, 838.

(19) Larson, A. C.; von Dreele, R. B. Report LAUR 86-748; Los Alamas National Laboratory: Los Alamos, NM, 1985.

(20) Fehlner, T. P. *Inorg. Chem.* **1973**, *12*, 98.

(21) Glavee, G. N.; Klabunde, K. J.; Sorensen, C. M.; Hadjipanayis, G. C. *Inorg. Chem.* **1995**, *34*, 28.

**Table 1.** Composition and Lattice Constant of the Hydrated Molybdenum Bronzes

| compound[a] | *a* (Å) | *b* (Å) | *c* (Å) |
|---|---|---|---|
| (a) $Na_{0.22}H_{0.03}(H_2O)_{0.43}MoO_3$ | 3.7435 | 19.2103 | 3.8515 |
| (b) $Na_{0.31}(H_2O)_{0.61}MoO_3$ | 3.74 | 19.21 | 3.86 |
| (c) $Na_{0.28}Ca_{0.09}(DMSO)_{0.52}(H_2O)_{0.60}MoO_3$ | 3.74(3.73) | 35.80(19.20) | 3.85(3.86) |
| (d) $Na_{0.28}Ca_{0.09}(DMSO)_{0.04}(H_2O)_{0.71}MoO_3$ | 3.74 | 19.12 | 3.86 |

[a] Compounds were prepared according to Thomas's method (a) and by the reduction of $MoO_3$ with $NaBH_4$ in $C_2H_5OH$ (b) and in DMSO after being dried in air for 2 days (c) and 12 days (d).

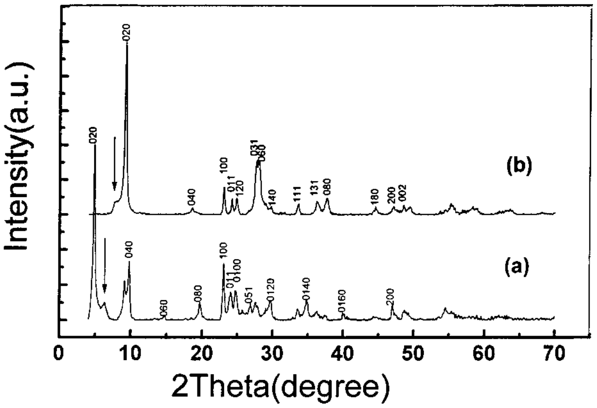
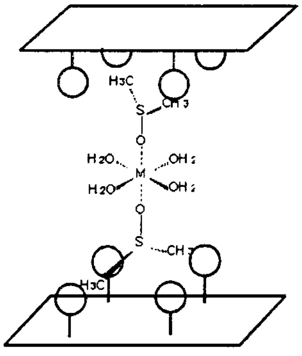


**Figure 2.** X-ray diffraction patterns of the hydrated molybdenum bronzes obtained by the reduction of $MoO_3$ with $NaBH_4$ in DMSO, after drying in air for 2 days (a) and 12 days (b). The un-indexed reflection in (a) with the interlayer spacing of about 9.6 Å is from DMSO-free hydrated molybdenum bronze. The peaks marked with arrows in the figure are from an unknown phase, which disappears after treating the samples with $H_2O$.

cation $(CH_3)_2S^+{-}O\cdots M(H_2O)_n\cdots O{-}S^+(CH_3)_2$ is oriented mostly perpendicular to the $MoO_3$ layers, as shown by **1**. The DMSO



**1**

intercalated molybdenum bronze is a metastable compound; the intercalated DMSO was gradually expelled from the materials when exposed to air. After 10 days in air, for example, almost all of the solvated DMSO was lost; hence, the interlayer spacing became identical to the DMSO-free hydrated molybdenum bronze (Figure 2b). In fact the product obtained in DMSO always contains considerable amounts of DMSO-free hydrated molybdenum bronze, as indicated in Figure 2a.

The reduction reaction rate in DMSO is much slower than that in ethanol; therefore, a longer reaction time is often needed to complete the reduction in DMSO. Table 2 summarizes the products and the reaction conditions in DMSO. Two facts should be noted. First, the reduction content of the products increases with the reaction time and the $NaBH_4/MoO_3$ ratio; a highly reduced molybdenum bronze was obtained after reaction for 2 months. The composition of this product is $Na_{0.10}Ca_{0.32}MoO_3{\cdot}0.08DMSO{\cdot}0.67H_2O$ with a cation-to-Mo ratio (M/Mo) of 0.42 and an averaged formal oxidation state of Mo of about +5.26. From our knowledge, this is the most reduced hydrated molybdenum bronze known so far that retains the $MoO_3$ layered structure. This compound is not stable and decomposes slowly in aqueous solution. Second, two different cations, $Na^+$ and $Ca^{2+}$, were present in the system; both can be intercalated into the molybdenum bronze during the reaction. At the initial stage, however, the intercalated cations were mainly the univalent cations, $Na^+$, and the intercalation of $Ca^{2+}$ occurred mainly as the reaction further proceeded. For example, after 7 days of reaction, the product $Na_{0.28}Ca_{0.09}(DMSO)_{0.52}(H_2O)_{0.60}MoO_3$ has a M/Mo ratio of about 0.37, which is almost as high as that in the most reduced product (M/Mo = 0.42). Meanwhile, the amount of the divalent cations is relatively lower (about 25%). Continuation of the reaction does not significantly change the M/Mo ratio, but the reduction content of the sample increases by partial replacement of $Na^+$ with $Ca^{2+}$, as indicated in the sample of $Na_{0.10}Ca_{0.32}MoO_3{\cdot}0.08DMSO{\cdot}0.67H_2O$. This observation implies that the maximum number of cation sites that can be used between the $MoO_3$ layers is about 0.4 per $MoO_3$ and that the molybdenum bronze tends to be formed as the cation sites are maximally occupied. Furthermore, the reduction rate is accelerated at higher temperature, as shown in Table 3. The reduction reaction rate is about 10 times higher at 100 °C than at room temperature.

Attempts to exchange $Na^+$ with $K^+$ or $Ca^{2+}$ were also made in DMSO and aqueous solution. The ion-exchange reaction in aqueous solution was efficient and could be completed in 1 h. In Table 4, we show the composition and the lattice parameters of the potassium and calcium molybdenum bronzes obtained by exchange reaction. The lattice constants *a* and *c* remain unchanged for the exchanged samples, while the lattice constant *b* varies accordingly with the cation size and the water content. The ion-exchange reaction in DMSO is similar to that in aqueous solution, unless a considerable amount of DMSO was intercalated into the compound. Additionally, the exchange reaction in DMSO is much slower than that in aqueous solution.

In addition to $H_2$, the gas released from the DMSO system contains $CH_3SCH_3$,[22] indicating that part of DMSO was reduced by $NaBH_4$ during the reaction. It is known that DMSO can be reduced to $CH_3SCH_3$ by a reducing agent such as $SnCl_2$, HI, or $LiAlH_4$ under refluxing conditions. To see if the released $CH_3SCH_3$ was formed by direct reduction of DMSO with $NaBH_4$, a DMSO solution of $NaBH_4$ was allowed to stand for a long period of time; but no $CH_3SCH_3$ was detected. Therefore, the reaction process in DMSO can be expressed as

$$2[MoO_3] + (2x)NaBH_4 \xrightarrow{DMSO} 2Na_x[MoO_3] + xB_2H_6 + xH_2 \qquad (6)$$

$$(CH_3)_2SO + 2NaBH_4 \xrightarrow{Na_xMoO_3} CH_3SCH_3 + B_2H_6 + H_2 + Na_2O \qquad (7)$$

The $MoO_3$ layers took up the electrons from $BH_4^-$ and became negatively charged and equivalent amounts of solvated

**Table 2.** Molybdenum Bonzes Obtained by Varying the Reacting Conditions

| compound | solvent | $NaBH_4/MoO_3$ (mole ratio) | $CaCl_2/MoO_3$ (mole ratio) | reaction time (h) | dry time in air (h) | M/Mo ratio | *d* (Å) |
|---|---|---|---|---|---|---|---|
| $Na_{0.25}(H_2O)_{0.50}MoO_3$ | ethanol | 0.5:1 | | 24 | 24 | 0.25 | 9.6 |
| $Na_{0.31}(H_2O)_{0.61}MoO_3$ | ethanol | 0.5:1 | | 36 | 24 | 0.31 | 9.6 |
| $Na_{0.15}Ca_{0.03}MoO_3{\cdot}0.79DMSO{\cdot}0.65H_2O$ | DMSO | 1:1 | 3:1 | 96 | 48 | 0.18 | 9.6<br>17.9 |
| $Na_{0.15}Ca_{0.07}MoO_3{\cdot}0.66DMSO{\cdot}0.86H_2O$ | DMSO | 1:1 | 3:1 | 120 | 48 | 0.22 | 9.6<br>17.9 |
| $Na_{0.20}Ca_{0.08}MoO_3{\cdot}0.63DMSO{\cdot}0.65H_2O$ | DMSO | 1:1 | 3:1 | 168 | 48 | 0.28 | 9.6<br>17.9 |
| $Na_{0.28}Ca_{0.09}MoO_3{\cdot}0.52DMSO{\cdot}0.60H_2O$ | DMSO | 1.5:1 | 3:1 | 168 | 48 | 0.37 | 9.6<br>17.9 |
| $Na_{0.28}Ca_{0.09}MoO_3{\cdot}0.04DMSO{\cdot}0.71H_2O$ | DMSO | 1.5:1 | 3:1 | 168 | 288 | 0.37 | 9.6 |
| $Na_{0.10}Ca_{0.32}MoO_3{\cdot}0.08DMSO{\cdot}0.67H_2O$ | DMSO | 1.5:1 | 3:1 | 1440 | 48 | 0.42 | 9.6 |
| complex | ethanol | 1:1 | | 36 | | | |
| complex | DMSO | 2.5:1 | 3:1 | 288 | | | |

**Table 3.** Temperature Dependence of the Reduction Reactions[a]

| temp (°C) | solvent | reaction time(h) | compound | reduction content (per $MoO_3$) |
|---|---|---|---|---|
| 25 | DMSO | 96 | $Na_{0.15}Ca_{0.03}MoO_3{\cdot}0.79DMSO{\cdot}0.65H_2O$ | 0.21 |
| 50 | DMSO | 24 | $Na_{0.18}Ca_{0.10}MoO_3{\cdot}0.58DMSO{\cdot}0.70H_2O$ | 0.38 |
| 100 | DMSO | 12 | $Na_{0.16}Ca_{0.10}MoO_3{\cdot}0.66DMSO{\cdot}0.72H_2O$ | 0.36 |

[a] The starting mixture contains 1 g of $MoO_3$ and 0.6 g of $NaBH_4$ with a mole ratio of 1:2.5.

**Table 4.** Composition and Lattice Constants of the Ion-Exchanged Molybdenum Bronzes

| composition | *a* (Å) | *b* (Å) | *c* (Å) |
|---|---|---|---|
| $K_{0.25}(H_2O)_{0.45}MoO_3$ | 3.74 | 21.60 | 3.85 |
| $Ca_{0.30}(H_2O)_{0.96}MoO_3$ | 3.73 | 25.90 | 3.92 |
| $K_{0.23}(H_2O)_{0.65}MoO_3$[4−7] | 3.74 | 22.70 | 3.78 |
| $K_{0.23}(H_2O)_{0.27}MoO_3$[4−7] | 3.68 | 18.64 | 3.83 |
| $K_{0.23}(H_2O)_{0.43}MoO_3$[4−7] | 3.46 | 21.50 | 3.87 |
| $MoO_3$ | 3.70 | 13.92 | 3.90 |

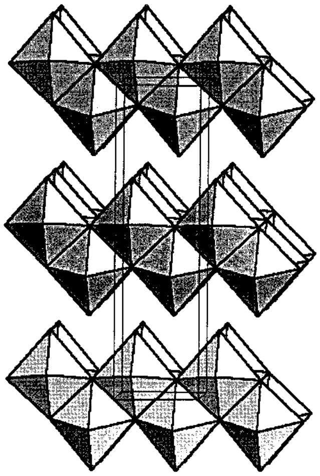


**Figure 3.** Crystal structure of $MoO_3$

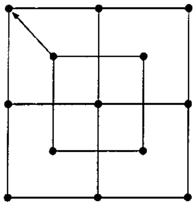
cations were intercalated between the $MoO_3$ layers, forming the solvated molybdenum bronze as shown in eq 6. After the $MoO_3$ layers were reduced to a certain extent, electron transfer from $MoO_3$ layers to DMSO occurred, which yielded $CH_3SCH_3$. Therefore, the formation of $CH_3SCH_3$ from DMSO is catalyzed by molybdenum bronze. The instability of DMSO in the molybdenum bronze can also be interpreted from the catalysis reaction of DMSO.

It should be noted that the reduction reactions of $MoO_3$ with $Na_2S_2O_4$ in aqueous solution are often accompanied by insertion of a proton. To obtain hydrated molybdenum bronzes, a large amount of $Na_2MoO_4$ has to be used as buffer to maintain a suitable pH of the aqueous solution; even then, a considerable amount of protons may be still present in the products.[2,3] In these organic solvents, the hydrolysis of $MoO_3$ and the intercalation of protons were prevented.

**Structure of Hydrated Molybdenum Bronze.** It has been well accepted that the hydrated molybdenum bronzes crystallize in an orthorhombic structure.[2,3] Depending on the ionic size, the intercalated cations may be located in octahedral or cubic sites between the $MoO_3$ layers.[1−7] To learn the structure details of the hydrated molybdenum bronze, we prepared sodium molybdenum bronze using Thomas's method and reinvestigated the structure model.

The X-ray powder diffraction pattern (Figure 1) was indexed with the orthorhombic cell proposed by Thomas et al.[2] ($a$ = 3.7435(4) Å, $b$ = 19.2103(7) Å, and $c$ = 3.8515(3) Å). The observed systematic absence of the reflections, $h + k = 2n$, reveals a *C*-centered orthorhombic cell with a possible space group of *C*222, *Cmm*2, or *Cmmm*. Note that the hydrated molybdenum bronze is topologically related to $MoO_3$. The structure of the $MoO_3$ layers should remain unchanged, and thus, the structure model can be constructed by shifting the $MoO_3$ layers accordingly with the observed symmetry.

Figure 3 shows the crystal structure of $MoO_3$ in which the double layer of molybdenum octahedra stack along the *b* axis, forming an orthorhombic layered structure. The interaction between the $MoO_3$ layers is mainly van de Waals force in nature. Note that the terminal oxygen atoms of the $MoO_3$ layer form a square net geometry; to maximize the van de Waals interaction between the layers, the terminal oxygen atoms of one $MoO_3$ layer are located just above the center of the adjacent square net, as shown by **2**. Between the $MoO_3$ layers exist octahedral



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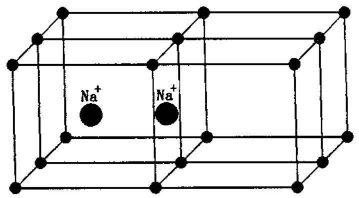

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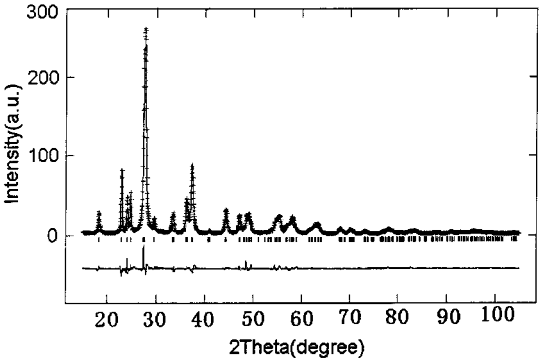

**Figure 4.** Rietveld profile fits for the $Na_{0.22}(H_2O)_{0.43}MoO_3$. The symbols are observed intensities. The solid line represents the calculated intensities. The tick marks indicate the position of the Bragg reflections. Differences between the observed and calculated intensities are shown at the bottom.

**Table 5.** Refined Structural Parameters of $Na_{0.22}(H_2O)_{0.43}MoO_3$

Space Group: *Cmmm*
$a = 3.7372(3)$ Å, $b = 19.183(1)$ Å,
$c = 3.8446(3)$ Å, $V = 275.62(4)$ Å$^3$
Rietveld Refinement: $R_p = 0.073$, $R_{wp} = 0.10$

| atom | site | *x* | *y* | *z* | occupation | $U_i/U_e \times 100$ |
|---|---|---|---|---|---|---|
| Mo | 4i | 0 | 0.32475(6) | 0 | 1 | 2.50(5) |
| O1 | 4i | 0 | 0.4144(3) | 0 | 1 | 2.6(2) |
| O2 | 4i | 0 | 0.3105(3) | $^1/_2$ | 1 | 2.6(2) |
| O3 | 4j | 0 | 0.2048(4) | 0 | 1 | 2.6(2) |
| Na | 2c | 0 | $^1/_2$ | $^1/_2$ | 0.44 | 2.4(5) |
| O4 | 2d | 0 | 0 | $^1/_2$ | 0.86 | 2.7(4) |

**Table 6.** Selected Bond Distances (Å) of $Na_{0.22}(H_2O)_{0.43}MoO_3$

| bond | in $Na_{0.22}(H_2O)_{0.43}MoO_3$ | in $MoO_3$ |
|---|---|---|
| Mo−O1 | 1.720(5) | 1.668 |
| Mo−O2 | 1.942(1) | 2.251 |
| Mo−O2 | 1.942(1) | 1.735 |
| Mo−O3 | 2.301(7) | 2.315 |
| Mo−O3 | 1.953(2) | 1.992 |
| Mo−O3 | 1.953(2) | 1.992 |
| Na−O1 | 2.528(4) | |
| Na−O4 ($H_2O$) | 1.8686(2) | |

and tetrahedral sites, but they are too small for the alkali metal ions. To create larger vacancies, the $MoO_3$ layers have to be shifted in the hydrated molybdenum bronze. One way of creating larger vacancies is to shift the adjacent layer along the diagonal direction of the square net $(^1/_2,0,^1/_2)$, which yields cubic vacancies between the layers as shown by **3**. The intercalated alkali metal ions may stay in the cubic sites or at the center of the vertical squares. For the latter case, other ligands, such as water, should be present in order to complete the octahedral coordination. Such a shift creates a mirror plane along the *b* axis so that the space group of the structure might be *Cmmm*.

Within the space group *Cmmm*, all of the atoms in the $MoO_3$ layers are located at the special positions, 4i $(0,y,0)$ and 4j $(0,y,^1/_2)$. The *y* values of the Mo and O atoms were derived from the structure of the $MoO_3$ layer and refined by Rietveld analysis of the X-ray diffraction data of $Na_{0.22}(H_2O)_{0.43}MoO_3$. At the initial stage, only the atoms in the $MoO_3$ layers were included in the refinement. Subsequent difference Fourier map analysis revealed considerable electron density at $(0,^1/_2,^1/_2)$ and $(0,0,^1/_2)$, which were assigned as $Na^+$ and $H_2O$, respectively. The occupation factors of these two positions were fixed according to the chemical analysis. The residual value of the final refinement is $R_p = 0.073$ and $R_{wp} = 0.10$. Figure 4 shows the Rietveld profile fits for $Na_{0.22}(H_2O)_{0.43}MoO_3$, and the refined structural parameters and selected bond distances are listed respectively in Tables 5 and 6. The crystal structure of $Na_{0.22}(H_2O)_{0.43}MoO_3$ is shown in Figure 5.

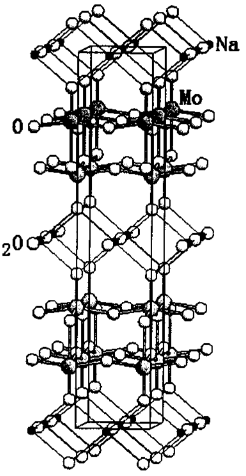

**Figure 5.** Crystal structure of the orthorhombic hydrated molybdenum bronze.

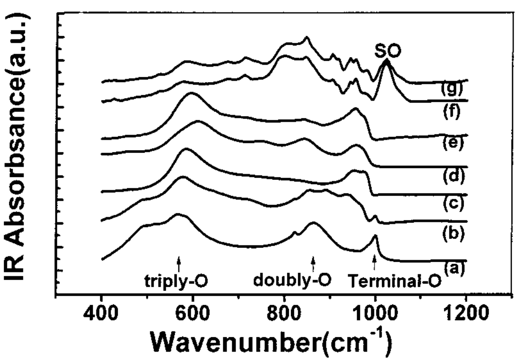

**Figure 6.** IR spectra of $MoO_3$ (a) and the molybdenum bronzes obtained by the reduction in EtOH: (b) $Na_{0.10}Ca_{0.03}(H_2O)_{0.25}MoO_3$, (c) $Na_{0.10}Ca_{0.05}(H_2O)_{0.28}MoO_3$, (d) $Na_{0.10}Ca_{0.05}(H_2O)_{0.51}MoO_3$, (e) $Na_{0.31}(H_2O)_{0.61}MoO_3$. IR spectra obtained by the reduction in DMSO: (f) $Na_{0.28}Ca_{0.09}(H_2O)_{0.60}(DMSO)_{0.52}MoO_3$, (g)$Na_{0.10}Ca_{0.32}(DMSO)_{0.08}(H_2O)_{0.74}MoO_3$

From the structure refinement it is clear that the framework of the $MoO_3$ was retained during the reaction, but the geometry of the Mo octahedron changed slightly. In $MoO_3$ the Mo is located close to an edge of the octahedron, resulting in two short and two long Mo−O bonds. While in $Na_{0.22}(H_2O)_{0.43}MoO_3$, the Mo is closer to a corner of the octahedron, resulting in an axially distorted octahedron. It is interesting to note that the coordination geometry of Mo in $Na_{0.22}(H_2O)_{0.43}MoO_3$ is similar to that found in the isoelectronic compound $H_{0.33}MoO_3$;[23] therefore, it might be the electron count that controls the distortion of the Mo coordination geometry.

The geometry change of the Mo coordination is further supported by IR spectra. Figure 6 shows the IR spectra of the molybdenum bronzes obtained in EtOH and DMSO. For comparison, the spectrum of $MoO_3$ is also included in the figure. The absorption band at about 1020 cm$^{-1}$ in Figure 6f,g originates from the stretching mode of the S−O group of DMSO in the material. In comparison with the pure DMSO solvent,[24] the IR band of S−O shifts about 80 cm$^{-1}$ to the low frequency. This means that the DMSO molecules are coordinated to the cations in the product. Three characteristic Mo−O IR bands in the $MoO_3$ layers are observed.[25,26] The band at about 997 cm$^{-1}$ is related to the terminal oxygen atoms, while the absorption bands at about 860 and 560 cm$^{-1}$ are related to the doubly and

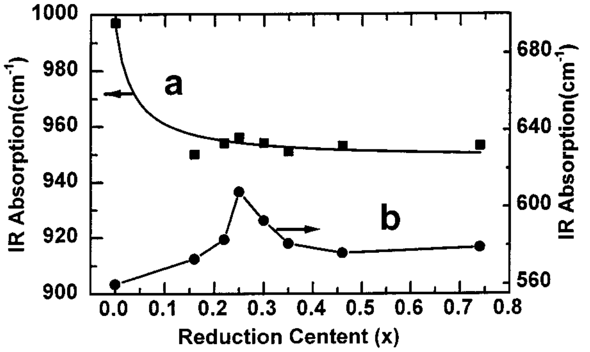

**Figure 7.** Variation of the IR absorption of Mo−O bond for the terminal (a) and triply bridged (b) oxygen atoms.

triply bridged oxygen atoms. In comparison with $MoO_3$, the vibration of the terminal oxygen shifts about 40 cm$^{-1}$ to the low frequency in the hydrated molybdenum bronze (Figure 6a−e), indicative of weakening of the terminal Mo−O bond. Interestingly, the shift of the terminal IR absorption occurs mainly at the initial stage of the reduction. When the reducing content is greater than 0.2 ($Mo^{5.8+}$), the IR absorption of the terminal oxygen remains at about 950 cm$^{-1}$ (Figure 7). In contrast, the IR absorption of the triply bridged oxygen shows unusual behavior; it has a red shift at the initial stage, then shows a blue shift when the reducing content is higher. The IR absorption of the doubly bridged oxygen also shows a red shift, but it disappears for the higher reduced samples. At present we can only say that the Mo−O bond changes with the reducing content; further study of the electronic structure will be helpful to understand the structural distortion in the reduced molybdenum bronzes. It is also worth noting that the characteristic IR absorption of the proton-intercalated molybdenum bronze (about 1001 cm$^{-1}$)[3,27] was not observed in the samples prepared in organic solvents; thus, the proton intercalation was indeed prevented in the organic solvents.

The structure model proposed by Thomas et al.[2] was based also on the fact that the intercalated cations occupy octahedral sites. However, the atomic arrangement within the $MoO_3$ layer is essentially different from present structure model. In their structure model, the mirror plane along the *b* axis is located within the $MoO_3$ layer, which leads to an unrealistic atomic arrangement in the $MoO_3$ layers. In the present structure model, the mirror plane is located between the $MoO_3$ layers, so the $MoO_3$ layer remains almost unchanged.

In the structure of $Na_{0.22}(H_2O)_{0.43}MoO_3$, the $Na^+$ ion is located at the center of the vertical square and two additional $H_2O$ molecules are needed to complete the coordination polyhedron. From structure refinement, the $H_2O$ molecules are located within a cube formed by the terminal oxygen atoms. However, the short Na−O4 distance implies that the $H_2O$ molecules may not necessarily be located at the center of the cube, which is highly disordered. Regarding the available sites in the structure, the M/Mo ratio should be less than 0.5 if the cations occupy mainly the octahedral site. On the other hand, the cubic sites are suitable for large cations, and the maximum M/Mo ratio may close to 0.5 if all of the cubic positions are occupied.

In conclusion, we have demonstrated that the hydrated molybdenum bronzes can be prepared by reduction of $MoO_3$ with $NaBH_4$ in ethanol and DMSO. Although the formed molybdenum bronze catalyzes the reduction reaction of DMSO, a highly reduced molybdenum bronze ($Mo^{5.26+}$) was obtained in the DMSO system. Reinvestigation of the structure model of the hydrated sodium molybdenum bronze revealed that a mirror plane is located between the $MoO_3$ layers and that furthermore the Mo octahedron is axially distorted possibly because of the electron-counting effect.

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(22) DMSO solution of $NaBH_4$ shows a characteristic IR absorption of the $BH_4^-$ group at about 2100−2300 cm$^{-1}$. As the reduction of $MoO_3$ proceeded, the intensity of this absorption decreased. In the meantime, the gas released from reaction system was collected and examined by MS, NMR, and FT-IR spectra. The experimental data (MS, *m*/*z* 62, 61, 47, 46, 45, 35; FT-IR, 3016 cm$^{-1}$; NMR, 2.0447 ppm) agree very well with the data for $CH_3SCH_3$.

(23) Adams, S.; Ehses, K.-H.; Spilker, J. *Acta Crystallogr.* **1993**, *B49*, 958.

(24) Weissberger, A. *Organic Solvents*, 3rd ed.; Wiley: New York, 1973; p 857.

(25) Olenkova, I. P.; Chumachenko, N. N.; Plyasova, I. M.; Tarasova, D. V.; Yurchenko, E. N. *React. Kinet. Catal. Lett.* **1983**, *22*, 339.

(26) Kerr, T. A.; Leroux, F.; Nazar, L. F. *Chem. Mater.* **1998**, *10*, 2588.

(27) Sotani, N.; Eda, K.; Sadamatsu, M.; Takagi, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 903.