

Characterization of Hydrated Sodium Molybdenum Bronzes

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Two kinds of hydrated sodium molybdenum bronzes, an air-dried bronze (AD) and a vacuum dried one (VD), are characterized using X-ray diffraction, TG-DTA, IR spectroscopy, and NMR. According to NMR results, the paired protons and a small amount of isolated protons fixed in position are included both in AD and VD. It is found that the hydrate-water (HW) in VD exists basically in the form of hydrated sodium ion, $\text{Na}^+(\text{H}_2\text{O})_2$, where Na^+ coordinates with four terminal oxygens of an (MoO_6) octahedron of MoO_3 and two oxygens of hydrate-water (HW-2). The composition of VD has been determined as $[\text{Na}(\text{H}_2\text{O})_{1.95}]_{0.22}\text{H}_{0.03}\text{MoO}_{3.11}$. In addition to HW-2, AD includes another hydrate-water (HW-1), which is easily removed by drying *in vacuo* and/or by standing in air. The composition of AD has been determined as $[\text{Na}(\text{H}_2\text{O})_{2+2.26}]_{0.23}\text{H}_{0.02}\text{MoO}_{3.10}$. © 1990 Academic Press, Inc.

Introduction

Interest in transition metal oxide bronzes has continued in recent years. Most of the interest has focused on the study of alkali metal molybdenum bronzes (1), because of their interesting physical properties such as highly anisotropic transport properties, superconductivity, and charge density wave-driven phase transitions. The sodium molybdenum bronze, $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$, was first prepared by Wold *et al.* (2) Ramanujachary *et al.* (3) have obtained highly crystalline $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ by a temperature gradient flux method. The sodium bronze usually has been prepared at temperatures above 800 K, when the fused salt electrolysis (2) or the temperature gradient flux method (3) was employed. However, we have found (4) that the sodium bronze could be obtained by heating the hydrated sodium bronze to temperatures less than 800 K in nitrogen.

The hydrated sodium molybdenum

bronze can be obtained by the reduction of MoO_3 with sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$, in aqueous solution. Schöllorn *et al.* (5) and Iwamoto *et al.* (6) have investigated the hydrated sodium bronze, but reached different conclusions regarding their composition. Schöllorn *et al.* have proposed that the composition of the hydrated sodium bronze is $(\text{Na}^+)_{0.5}(\text{H}_2\text{O})_n[\text{MoO}_3]^{0.5-}$. Iwamoto *et al.* have proposed the composition of $[(\text{Na}^+)_{0.25}(\text{H}^+)_{0.25}(\text{H}_2\text{O})_n][\text{MoO}_3]^{0.5-}$. On the other hand, Son *et al.* (7) have reported the existence of $\text{Na}_{0.5}(\text{H}_2\text{O})_n\text{MoO}_3$. Recently, Thomas and McCarron (8) have obtained two kinds of hydrated sodium bronzes. One is an air-dried proton free hydrate bronze (AD) and the other, a proton free hydrated bronze (VD) which has been obtained from AD by drying *in vacuo*. They have studied the hydrate-water by thermogravimetry and have determined the composition of $[\text{Na}(\text{H}_2\text{O})_5]_{0.25}\text{MoO}_3$ for AD and of $[\text{Na}(\text{H}_2\text{O})_2]_{0.25}\text{MoO}_3$ for VD.

As mentioned previously (4), $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ has been obtained at low temperature from the hydrated sodium bronze. Therefore, it is important to know why the sodium bronze can be formed from the hydrated bronze at such low temperature. First of all, we studied the hydrated sodium bronze. The location and behavior of the hydrate-water (denoted as HW) are of much interest. Then we tried to investigate HW included in two types of hydrated bronzes using X-ray diffraction, TG-DTA, IR spectroscopy, and NMR. We report in the present paper the detailed characterization of the hydrated sodium molybdenum bronze and discuss the location and the behavior of HWs.

Experimental

Sample Preparation

Synthesis methods were similar to those described previously (5, 8). MoO_3 powder (99.95%) (Climax Molybdenum Asia Limit.) was calcined at 973 K in air for 2 hr. MoO_3 (5 g) was suspended in 250 ml of distilled water at 276–278 K. A mixture of $\text{Na}_2\text{S}_2\text{O}_4$ (2 g) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (60 g) was divided into several portions, which were introduced into the suspended solution every 15 min. During the reaction nitrogen gas was passed through the solution to prevent oxidation of the product. The product was collected by suction filtration and was washed with water until the filtrate was colorless. The product that was air-dried at room temperature is labeled "AD," and the one dried at room temperature *in vacuo* overnight is designated "VD."

Characterization

X-ray studies. Samples were mixed with an internal standard (ca. 5 wt% Si powder). All powder X-ray diffraction patterns were performed using a Rigakudenki Geiger D-1 Flex diffractometer with $\text{CuK}\alpha$ radiation.

TG-DTA studies. TG-DTA curves were obtained using a MAC Science TG-DTA 2000 with a heating rate of 10 K min^{-1} .

IR studies. IR spectra were obtained using a JASCO 701G spectrophotometer.

NMR studies. Proton NMR spectra were obtained at room temperature and at 77 K by a home-built pulsed NMR spectrometer operating at 11 MHz. Absorption spectra were obtained by the Fourier transformation of FID (free induction decay) signals. The zero-time-resolution method (ZTR) (9) was utilized together with the ordinary FID method, because the Fourier transform of FID was usually distorted owing to the lack of the initial part of FID during the dead time of the receiver after an intense rf pulse. The ZTR was performed by applying a 90° phase-shifted 90° pulse following after the first 90° pulse, a solid echo signal being observed. The lack of the initial parts of FIDs were made up by the corresponding parts of the solid echo signals. The signals were integrated and averaged by an averager to improve the signal to noise ratio.

Chemical Analyses

The Na and Mo contents in the samples were measured using a Hitachi 180-80 atomic absorption spectrometer using the 330.23-nm line for Na and the 313.26-nm line for Mo. Mo^{5+} was determined by the Choain and Marion method (10).

Results

Figure 1 shows the X-ray diffraction patterns of the samples. The patterns of the sample that was air-dried and the sample that was vacuum-dried overnight were identical with those of AD and VD bronze reported by Thomas and McCarron (8), respectively. According to the X-ray results, it was found that AD was unstable. The X-ray powder diffraction of an AD sample standing in air for 3 days at room temperature

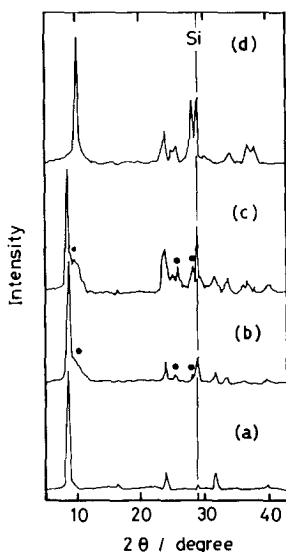


FIG. 1. X-ray diffraction patterns of (a) AD, (b) after standing for 3 days, (c) for 10 days, and (d) for 30 days (VD). (●) gives the pattern attributed to VD.

shows lines (marked with ● in the figure) attributed to VD. As the length of air exposure increased, VD gradually increased and, finally, the sample was completely transformed to VD after 30 days. The diffraction pattern of this material was identical with that obtained by drying AD *in vacuo* overnight. However VD did not change to AD, even though it was allowed to stand in moisture.

TG-DTA curves of AD and VD are shown in Fig. 2. AD gives two endothermic peaks at 338 and 450 K with weight losses of 5.5 and 4.9 wt%, respectively. This suggests that two kinds of HW exist. HW removed at low temperature (the first step) is designated as HW-1 and that at high temperature, as HW-2. AD heated after the endothermic peak at 420 K gives an X-ray pattern identical with that of VD. VD shows an endothermic peak at 442 K with a weight loss of 5.1 wt%, which corresponds to that of HW-2. The TG curve of VD shows that the removal of HW-2 began at room temperature.

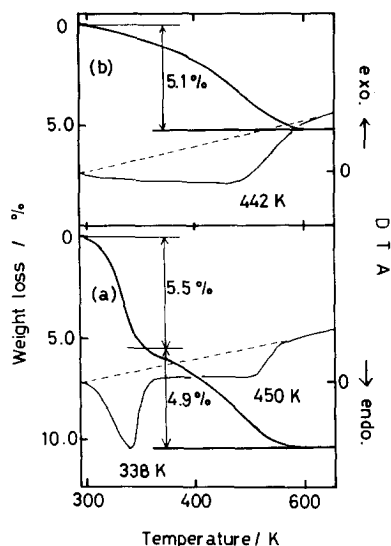


FIG. 2. TG-DTA curves of (a) AD and (b) VD.

Figure 3 shows the IR spectra of AD and VD. The absorption band due to an OH group might have been expected, because HWs are included in AD and VD. As AD and VD are dark blue in color and have high electrical conductivity (7), the intensity of the IR bands is very weak. Therefore, we could not detect the band due to the OH group. AD shows bands at 955 and 565 cm^{-1} and VD, at 970 and 570 cm^{-1} . No significant difference was observed between the bands of AD and VD, but the frequencies of AD

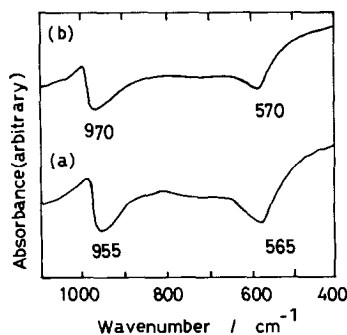


FIG. 3. IR spectra of (a) AD and (b) VD.

TABLE I
RESULTS OF CHEMICAL AND TG ANALYSES OF AD
AND VD

		HW-1	HW-2	Mo	Na ⁺	O	x(Mo ⁵⁺)	H ⁺
	%	5.50	4.90	56.99	3.14	29.46		
AD	(a)	0.52	0.46	1.00	0.23	3.10	0.25 (d)	0.02 (e)
	(b)	2.26	2.00	4.35	1.00			
	(c)			4.00			1.00	
	%		5.10	60.36	3.33	31.21		
VD	(a)		0.43	1.00	0.22	3.11	0.25 (d)	0.03 (e)
	(b)		1.95	4.55	1.00			
	(c)			4.00			1.00	

Note. (a) Ratio to Mo; (b) ratio to Na; (c) Mo/x ratio. (d) Determined by the Choain and Marion method (10). (e) Obtained from $x(\text{Mo}^{5+}) - \text{Na}^+/\text{Mo}$.

are lower by 5–15 cm^{-1} than those of VD. This suggests that these shifts may result from the presence of HWs. The bands at 955 and 970 cm^{-1} are assigned to a Mo=O double bond and those at 565 and 570 cm^{-1} , to an Mo—O single bond.

The results of TG and chemical analyses are shown in Table I. The quantity of Mo⁵⁺ per MoO₃, x , in both AD and VD was determined to be 0.25, which corresponds to that of cations in the samples. The Na/Mo ratios in AD and VD are 0.23 and 0.22, respectively. On the other hand, H₂O/Mo ratios for HW-1 and HW-2 in AD are found to be 0.52 and 0.46. The ratios of H₂O/Na are 2.26 for HW-1 and 2.0 for HW-2, respectively. The H₂O/Mo ratio of HW-2 in VD is 0.43 and, therefore, the H₂O/Na ratio is 1.95. The ratio for HW-1 in AD is found to be variable within a small range, but that for HW-2 is nearly constant and independent of the condition of preparation.

Figure 4 shows NMR spectra of samples, which were observed at room temperature and at 77 K. Figure 4a shows a typical spectrum of AD at room temperature. VD shows a spectrum similar to that of AD. Both spectra are narrowed by a motion and slightly asymmetric about the frequency of the peak. This result suggests that all H₂O molecules travel or rotate between the MoO₃ layers at room temperature. Similar spectra are observed on hydrogen molybdenum

bronzes reported previously (11–14). The spectrum of AD at 77 K is considered to be a superposition of two components, a narrow line and a broader one with side peaks. The broad line is similar to the "Pake-doublet," which is attributed to proton pairs (15). The central peak is a Gaussian like line arising from isolated protons fixed in position. The spectrum of VD also exhibits the Gaussian like line and the Pake-doublet. However, the apparent area of the Pake-doublet is smaller than that of AD, which suggests that the quantity of paired protons in VD is smaller than that in AD. The TG result supports this.

The distance r between the paired protons can be calculated approximately from the side-peak separation, ΔH , by applying a formula, $\Delta H = 3\gamma\hbar/2r^3$. The observed values of $\Delta H = 11.8$ Oe for AD and 10.6 Oe for VD yield $r = 0.153$ and 0.159 nm, respectively. These values are almost equal to the proton-proton distance 0.158 nm of H₂O in CaSO₄ · 2H₂O (15). Therefore, both paired protons are attributed to hydrate-water.

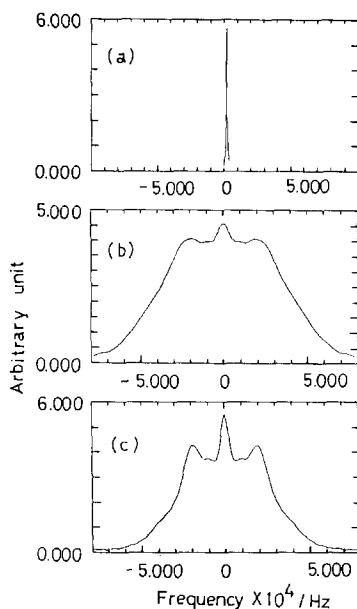


FIG. 4. NMR spectra of (a) AD at room temperature, (b) AD at 77 K and (c) VD at 77 K.

Discussion

The hydrated sodium molybdenum bronze is formulated as $[\text{Na}(\text{H}_2\text{O})_n]_x[\text{MoO}_3]$. According to chemical and TG results as shown in Table I, AD is formulated as $\text{Na}_{0.23}(\text{H}_2\text{O})_{0.98}\text{MoO}_{3.10}$ and VD, as $\text{Na}_{0.22}(\text{H}_2\text{O})_{0.43}\text{MoO}_{3.11}$. Schöllhorn *et al.* (5), Iwamoto *et al.* (6), and Son *et al.* (7) proposed the $[\text{MoO}_3]^{0.5-}$ layers. On the contrary, Thomas and McCarron (8) proposed the $[\text{MoO}_3]^{0.25-}$ layers. However, both $[\text{MoO}_3]^{0.5-}$ and $[\text{MoO}_3]^{0.25-}$ layers are the same structure derived from edge sharing (MoO_6) octahedra. The difference is due to the electron charge of the layers. The former proposed the presence of H^+ and the latter did not. In the present work, as shown in Table I, the ratio of Mo^{5+}/Mo is 0.25 for both samples. These results support the conclusion that both AD and VD consist of $[\text{MoO}_3]^{0.25-}$ layers.

The observed HW-2/ Na^+ ratios of 1.95–2.00 are nearly constant, even though the method of preparation is different. This implies that two H_2O molecules are associated with one Na^+ ion to yield a hydrated sodium ion such as $\text{Na}^+(\text{H}_2\text{O})_2$. HW-2 is stable up to about 600 K as shown in Fig. 2. On the contrary, the HW-1/ Na^+ ratio is 2.26 in the present work and is found to be variable depending upon the method of preparation, although Thomas and McCarron proposed the ratio 3. Moreover, HW-1 is removed completely by heating below 373 K or by standing in air for 30 days as shown in Fig. 1.

A linear structure arrangement such as $\text{H}_2\text{O}-\text{Na}^+-\text{OH}_2$ can be considered for $\text{Na}^+(\text{H}_2\text{O})_2$ in VD, where the waters of hydration correspond to HW-2. The length and the cross-section of this model can be roughly estimated from the radii of their components. The radius of the Na^+ ion is 0.116 nm for 6-coordination and 0.113 nm for 4-coordination (16). A gaseous H_2O molecule is usually represented by using van der Waals radii of hydrogen and oxygen atoms.

TABLE II
INTERLAYER SPACINGS, d_{020} , OF AD AND VD

	AD		VD	
	d (nm)	Δd (nm) ^a	d (nm)	Δd (nm) ^a
Schöllhorn (5)	1.141 ^b	0.449	0.956 ^c	0.264
Iwamoto (6)	1.138 ^d	0.446		
Thomas (8)	1.148	0.456	0.963	0.271
Present work	1.118	0.426	0.953	0.261

^a $\Delta d = d_{020} - d_{020}(\text{MoO}_3 = 0.692 \text{ nm})$.

^b The sample corresponding to AD has the composition of $(\text{Na}^+)_{0.5}(\text{H}_2\text{O})_n[\text{MoO}_3]^{0.5-}$.

^c The sample was dried at 298 K under a vacuum of 10^{-2} Torr, which corresponds to VD.

^d The sample corresponding to AD has the composition of $(\text{Na}^+)_{0.25}(\text{H}^+)_{0.25}(\text{H}_2\text{O})_n[\text{MoO}_3]^{0.5-}$.

According to the calculation, the length is 0.319 nm and the cross-section, 0.319×0.392 nm. If we estimate the length and the cross-section of H_2O by using the covalent bond radii of hydrogen and oxygen atoms (17), we obtain 0.163 nm and 0.163×0.212 nm, respectively. If we adopt 6-coordination for the Na^+ ion (16), the length and the cross-section for the model of $\text{H}_2\text{O}-\text{Na}^+-\text{OH}_2$ are 0.558 nm and 0.558×0.232 nm when the covalent bond radii are used, and 0.870 nm and 0.870×0.392 nm when van der Waals radii are used, respectively.

A measure of whether a guest ion can penetrate into the MoO_3 layers should depend on an interlayer spacing. The value of d_{020} indicates a characteristic interlayer spacing. The d_{020} value obtained from X-ray diffraction patterns of VD is 0.953 nm, which is a little smaller than the others as shown in Table II. This means an expansion of the interlayer spacing of the starting material, MoO_3 ($d_{020} = 0.692$ nm) (18). The degree of this expansion is evaluated by the value of Δd , which is obtained by subtracting the interlayer spacing of MoO_3 from the observed d_{020} . The Δd is 0.261 nm for VD as shown in Table II. This value permits only $\text{H}_2\text{O}-\text{Na}^+-\text{OH}_2$, which is assumed by using covalent bond radii to be included between the layers. On the other hand, the

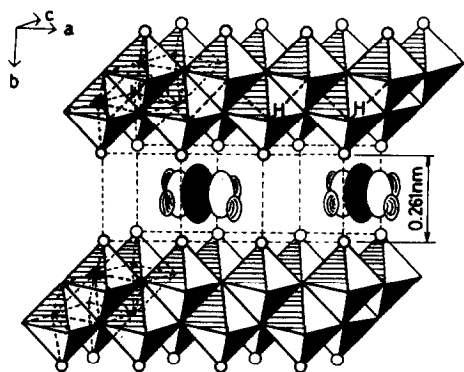


FIG. 5. Model of VD. The hydrated sodium ion, $\text{H}_2\text{O}-\text{Na}^+-\text{OH}_2$, is located between the MoO_3 layers perpendicular to the b -axis. (●) Na^+ ion, (⊙) hydrogen atom and (○) oxygen atom in H_2O , (○) terminal oxygen. Shaded circles represent oxygen atoms common to three MoO_6 octahedra. H represents an isolated proton is fixed in position between vertex-sharing oxygen atoms along the zig-zag line (---).

lattice constant of VD is $a = 0.3876$ nm (8) and the length of $\text{H}_2\text{O}-\text{Na}^+-\text{OH}_2$ (0.558 nm) along the a -axis just falls in the range of twice the lattice constant, $2a$ (0.7752 nm). That is, $\text{H}_2\text{O}-\text{Na}^+-\text{OH}_2$ needs two unit cells. This consideration supports the model by Thomas and MaCarron (8). As the Na^+ ion has 6-coordination, 4 of them are connected with 4 terminal oxygens of the MoO_3 layers and 2 with 2 oxygens of HW-2 as shown in Fig. 5. According to this model, $\text{H}_2\text{O}-\text{Na}^+-\text{OH}_2$ coordinates with four (MoO_6) octahedra of MoO_3 layers. If $\text{H}_2\text{O}-\text{Na}^+-\text{OH}_2$ occupies all available sites of VD, the $\text{Na}^+(\text{H}_2\text{O})_2/\text{Mo}$ ratio is 0.25. This supports the results of chemical analysis that suggested that the $[\text{MoO}_3]^{0.25-}$ layers are formed, as mentioned above.

As shown in Table I, there is a difference between the ratios of Na^+/Mo and Mo^{5+}/Mo . The Na^+/Mo ratio is smaller by 0.03 in VD. This suggests the presence of protons. NMR results mentioned above show the central peak in both AD and VD, which can be attributed to a small amount of isolated protons fixed in position. It is well known

(14) in the case of hydrogen molybdenum bronzes that protons occupy first the available sites between the intralayer position, connecting the vertex-sharing oxygen atoms along the zig-zag line as shown in Fig. 5. Moreover, it is confirmed (19) that the hydrated sodium bronze can be protonated, depending upon the preparation condition. Therefore, the composition of VD obtained in this work is formulated as $[\text{Na}(\text{H}_2\text{O})_{1.99}]_{0.22}\text{H}_{0.03}\text{MoO}_{3.11}$ and it is reasonable that the composition of completely proton free VD is $[\text{Na}(\text{H}_2\text{O})_2]_{0.25}\text{MoO}_3$.

In addition to HW-2, AD contains additional water which has been designated as HW-1. It is important to know the possible locations of HW-1. The Δd of AD is 0.426 nm and is larger by 0.165 nm than that of VD. As has been described in the sample preparation, AD is formed in aqueous solution. In the solution, $\text{Na}^+(\text{H}_2\text{O})_n$ is produced and penetrates into the MoO_3 layers by expanding the layers. There is no difference among HWs of $\text{Na}^+(\text{H}_2\text{O})_n$ in aqueous solution. However, when they are inserted into the MoO_3 layers, the difference should occur as shown in the TG-DTA results. TG-DTA results for AD clearly show the presence of two kinds of HWs. NMR peaks in AD are broader than in VD, which is consistent with this result. In aqueous solution, it has been suggested that the Na^+ ion is surrounded by six H_2O molecules (20). According to others (21-23), $\text{Na}^+(\text{H}_2\text{O})_n$ has a value of $n = 2.8-4.5$. Thus, Na^+ ion is not fully coordinated with six H_2O molecules. An approximate radius of the hydrated sodium ion is 0.276 nm (24), which is almost equal to 0.279 nm, one half of the length of $\text{H}_2\text{O}-\text{Na}^+-\text{OH}_2$ evaluated by using the radius of the covalent bond. If $\text{Na}^+(\text{H}_2\text{O})_n$ with $n = 2.8-4.5$ is assumed to be spherical, the radius is 0.279 nm. The length is 0.558 nm, which is larger than Δd (0.426 nm) of AD. In this case, it is impossible that $\text{H}_2\text{O}-\text{Na}^+-\text{OH}_2$ is inserted parallel to the b -axis. In addition, the lattice constant c

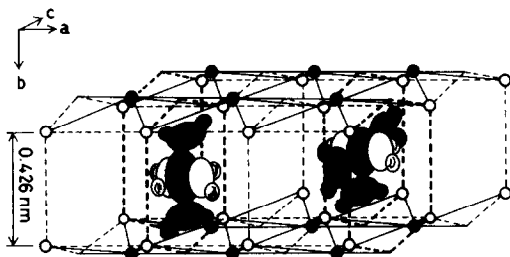


Fig. 6. Model of AD. H_2O molecules which are perpendicular to the b - and c -axes correspond to HW-1. Shaded circles represent terminal oxygen. (○) Oxygen atom common to three MoO_6 octahedra, (●) Na^+ ion, (⊙) hydrogen atom and (○) oxygen atom in H_2O . A shaded H_2O molecule corresponds to HW-1. A bold dashed line (---) combines the central terminal oxygens of two units.

of AD is 0.375 nm. This value is also too small for $\text{H}_2\text{O}-\text{Na}^+-\text{OH}_2$ to be inserted parallel to the c -axis. However, as mentioned above, when $\text{Na}^+(\text{H}_2\text{O})_2$ ions are included between the interlayers, they need the set of four terminal oxygens and must be located in the center of every other set, as shown with the bold dashed line in Fig. 6.

From the above considerations we propose a model as follows: two HWs, which correspond to HW-2, are perpendicular to the b -axis and interact rather strongly with terminal oxygens in the outer sides of two units. Contrary to this, from consideration of the structure of (MoO_6) octahedra and by assuming a 6-coordination state for the Na^+ ion, the residual HWs, which correspond to HW-1, may be oriented perpendicular to the b - and c -axes. As these HW-1s are close to four terminal oxygens in the central set, some weak repulsion may take place between the terminal oxygens and HW-1s. Consequently, HW-1 becomes easy to remove even standing in room ambient temperature.

As in the case of VD, AD obtained in this work contains a small amount of protons (0.02) and, therefore, is formulated as $(\text{Na}^+)_{0.23}(\text{H}^+)_{0.02}(\text{H}_2\text{O})_{2+2.26}\text{MoO}_{3.10}$. It is

reasonable that the composition of completely proton free AD is $[(\text{Na}(\text{H}_2\text{O})_{2+n'})_{0.25}\text{MoO}_3]$, where n' is more than 2.

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