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Preparation and Structure of Manganese Molybdates

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Manganese molybdates were prepared by precipitation in aqueous solution. Several monohydrates were obtained in the pH range 3–8. A yellow precipitate that formed initially is also a monohydrate but transforms at 60–100 °C into other, more crystalline, products depending upon pH. The compound obtained at pH 7–8 is triclinic, with $a = 5.776$ (4) Å, $b = 5.964$ (4) Å, $c = 6.992$ (4) Å, $\alpha = 100.32$ (5)°, $\beta = 95.56$ (5)°, $\gamma = 106.81$ (5)°, and $Z = 2$. The structure consists of molybdate tetrahedra and Mn(II) octahedra in which the tetrahedra share four corners with four different octahedra. The water molecule is coordinated to the manganese. Heating any of the hydrates to elevated temperatures converts them to the α-$MnMoO_4$ phase. In contrast, hydrothermal treatment of the hydrates at 200 °C transforms them to an anhydrous product with the $NiWO_4$ structure. A compound, $Na_2Mn_2(MoO_4)_3 \cdot 3H_2O$, was prepared from alkaline solution. Hydrothermal treatment at 200 °C converted it to $NaMn_2(OH)(H_2O)(MoO_4)_2$. The structure of this latter phase confirmed the bridging scheme proposed earlier, as it was possible to locate the positions of the hydrogen atoms.

Introduction

First-row transition-metal molybdates represent an interesting group of related compounds because of their magnetic[1] and catalytic[2,3] properties and their spectral features.[4] The molybdates may be prepared by solid-state reactions of MoO_3 with the transition-metal oxides[4,5] or by precipitation from aqueous solutions of soluble salts.[6,7] Several of these preparations have been used to catalyze such reactions as the oxidation of alkenes and the decomposition of formic acid. In previous papers we described the preparation of zinc molybdates from aqueous solution and their crystal structures.[8,9] The solution preparations were found to be basic sodium zinc molybdates in contrast to the zinc orthomolybdates produced at high temperatures. It was therefore of interest to examine the behavior of other transition-metal species in this series. In this paper we describe the preparation and structures of some Mn(II) molybdates.

The reaction of MoO_3 with $MnCO_3$ or MnO yields $MnMoO_4$.[4,5] The same product is obtained when Mn_2O_3 or MnO_2 is used as the source of manganese as these oxides lose oxygen in the process of heating at 400–600 °C.[5] The crystal structure of α-$MnMoO_4$ has been determined by Abrahams and Reddy.[10] In this structure the Mn atoms are octahedrally coordinated by oxygen while the molybdate species is tetrahedral.

Corbet and Eyraud[6] reported the synthesis of $MnMoO_4 \cdot 0.9H_2O$. Pezerat[7] found that this compound was isomorphous with similar Zn, Ni, and Co salts. He speculated on the possibility of disorder in these compounds resulting from the deficit of water molecules. In contrast, other workers[11] obtained $MnMoO_4 \cdot 1.5H_2O$ when an ammonium molybdate solution was added to $MnSO_4$ and the precipitate digested for 45 min at 80–90 °C. The water was lost in two steps, 1 mol at ~290 °C and the remaining $^1/_2$ mol at 380 °C. The X-ray powder pattern of this molybdate heated to 625 °C did not correspond to the phase described by Abrahams and Reddy.[10,12] Since the behavior of a catalyst is dependent upon its structure and degree of crystal perfection, among other factors, it was of interest to better identify and characterize the manganese molybdate phases. This was rarely done in the reported catalytic studies.[13]

Sleight and Chamberland[14] prepared manganese molybdates by four different methods, all at elevated temperatures. When the reaction was carried out at ambient pressures, the product was always α-$MnMoO_4$ as described by Abrahams and Reddy. However, the solids obtained from high-pressure reactions had the $NiWO_4$ structure.[15] Manganese(II) is also known to form a molybdate of the type $Mn_2Mo_3O_8$ at high temperatures under reducing conditions.[16] However, lower valent molybdenum oxides will be discussed in a separate paper as we have found nonstoichiometry in these compositions due to the presence of Mo(V).

Experimental Section

Preparation of Manganese(II) Molybdates. All of the chemicals used were ACS reagent grade, and distilled, deionized water was used throughout. Three different compounds of composition $MnMoO_4 \cdot H_2O$ were prepared under different conditions.

(1) A 100-mL portion of a 1 M $Na_2MoO_4 \cdot 2H_2O$ solution was brought to a boil in a three-neck round-bottom flask. To this solution was added 100 mL of a 1 M $MnSO_4 \cdot H_2O$ solution, dropwise with stirring through a separatory funnel. A white-yellow precipitate formed immediately, but when the solution was refluxed, it turned beige. Refluxing was continued for 2 days to ensure good crystallinity in the product. The pH of the solution was 7.1. The precipitate was filtered off, washed free of sulfate ion, and dried in a desiccator to constant weight. The order of addition of the reagents made no difference in the final product.

(2) The preparation described in (1) above was repeated at room temperature, but the pH was conrolled at 4. This was achieved by initially adjusting the pH of the manganese sulfate solution to 4 with 1 M H_2SO_4, monitoring the pH as the basic reagent was added, and adjusting it with sulfuric acid. When all the molybdate had been added, the mixture was refluxed for 2 days. A beige precipitate was recovered and treated as in (1). Variations in pH from 3 to 5.2 produced the same compound. No precipitate was obtained below pH 3, and when the pH was close to 3, several hours of refluxing were required for a precipitate to form.

(3) Preparation 2 was repeated, but the pH was maintained at 5.5. A white-yellow precipitate formed, which turned light brown after about 7 h of refluxing. The total reflux time was 18 h, after which the solid was recovered. Analytical data for all three preparations are given in Table I.

$Na_2Mn_2(MoO_4)_3 \cdot 3H_2O$. In this preparation 100 mL of 2 M sodium molybdate was added to 50 mL of 1 M manganese(II) sulfate as described in (1) above. A light yellow precipitate formed immediately and was refluxed in the mother liquor for 24 h. The pH of the solution was 7.8. Elemental analysis of the recovered, dried solid is given in Table I. When this mixture was refluxed for 2 days or more, a small amount of brown crystals formed on the walls of the flask above the liquid level. These proved to be $MnMoO_4 \cdot H_2O$, as prepared in (1), and the crystals were large enough for X-ray structure determination.

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Table I. Molar Ratio and Percent Weight Loss for Products **1**–**4**

		elemental anal., mmol				
pH of ppt	product	Na	Mn	Mo	% weight loss (TGA)	% water loss (calcd)
7.1	$MnMoO_4 \cdot H_2O$ (**1**)		0.024	0.022	7.6 (360 °C)	7.7
4	$MnMoO_4 \cdot H_2O$ (**2**)		0.020	0.019	7.1 (325 °C)	7.7
5.5	$MnMoO_4 \cdot H_2O$ (**3**)		0.023	0.027	4.4 (270 °C)	
					7.8 (total) (350 °C)	7.7
7.8	$Na_2Mn_2(MoO_4)_3 \cdot 3H_2O$ (**4**)	0.013	0.014	0.022	3.9 (200 °C)	
					7.5 (total) (285 °C)	7.8

Hydrothermal Reactions. Hydrothermal reactions were run as a means of growing larger single crystals for X-ray structure work.[8] $MnMoO_4 \cdot H_2O$ (**1**) was mixed with 10 mL of 2 M sodium molybdate and heated in a 71-mL Parr bomb (Teflon lined) at 200 °C for 24 h. This produced yellow-green crystals of $NaMn_2(OH)(H_2O)(MoO_4)_2$ as shown by X-ray analysis. The same phase was obtained in the hydrothermal treatment of $Na_2Mn_2(MoO_4)_3 \cdot 3H_2O$ for 24 h. The hydrothermal reaction of $Na_2Mn_2(MoO_4)_3 \cdot 3H_2O$ or any of the hydrated manganese molybdates with 1 M Na_2MoO_4 for 3 days at 200 °C and autogenous pressure yielded brown needle-shaped crystals of $MnMoO_4$ that had the $NiWO_4$ structure (X-ray analysis). In some instances mixtures of $NaMn_2(OH)(H_2O)(MoO_4)_2$ and $MnMoO_4$ were obtained.

Analytical and Instrumental Details. A small amount (~0.1 g) of each prepared manganese molybdate was dissolved in concentrated H_2SO_4 and diluted to 100 mL with water. The solutions were then analyzed for Na, Mn, and Mo by the inductively coupled plasma (ICP) technique. Standards were prepared as sodium sulfate, manganese sulfate, and sodium molybdate solutions. The results are given in Table I. The water content of each sample was determined by thermogravimetric analysis (Cahn RG unit) at a heating rate of 4°/min under a nitrogen atmosphere.

X-ray powder patterns were obtained with Cu Kα filtered radiation on a Seifert-Scintag PAD-II automated powder diffractometer. IR spectra of all of the samples were taken with a Perkin-Elmer 580B spectrometer. These spectra were used mainly to determine the presence of H_2O and OH groups and to see the changes resulting from dehydration.

X-ray Single-Crystal Data Collection and Treatment. X-ray intensity data were collected on a CAD-4 computer-controlled κ-axis diffractometer (Enraf-Nonius) at ambient temperatures. The instrument was equipped with an incident beam graphite crystal monochromator, and Mo radiation was used (λ = 0.71073 Å). Data were collected by the ω–2θ method to 80.0° 2θ. Scan speeds varied from 20°/min for the reflections with the highest intensities to approximately 2°/min for the weakest reflections. The angular scan width was $A + 0.347(\tan \theta_{\lambda\alpha_2})$, where $\theta_{\lambda\alpha_2}$ is determined from the formula

$$\theta_{\lambda\alpha_2} = \theta_{\lambda\alpha_1} + \frac{\lambda\alpha_2 - \lambda\alpha_1}{\lambda\alpha}\frac{360}{2\pi}(\tan \theta_{\lambda\alpha_1})$$

and A depends on the crystal mosaic spread and on the divergence of the primary beam. A for these structures was 0.70. The scan was extended on each side of the peaks by 25% for background determination. Accurate unit cell parameters were determined from 25 reflections collected at high 2θ angles ($2\theta > 30°$).

Three standard reflections were measured approximately every 150 reflections as a check of crystal and electronic stability; only statistical variations of these intensity standards were observed. Data were corrected for Lorentz and polarization effects. A series of ψ scans were used to empirically correct for absorption. The important crystal information for the three structures is listed in Table IV.

Structure Solution and Refinement. The structures were solved by three-dimensional Patterson methods, which yielded the positions of the molybdenum and manganese atoms. Successive difference Fourier syntheses yielded the remaining atoms. All of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods; the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/[\sigma(F_o^2)]$ and only the data having $I > 3\sigma(I)$ were included in the refinement. The standard deviation on intensities, $\sigma(I)$, is defined as $\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}/Lp$, where S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarization factor, and p is an instrumental factor that in this case was 0.05.

Table II. X-ray Powder Patterns of Manganese Molybdates Prepared in Aqueous Media

$MnMoO_4 \cdot H_2O$ (**1**)		$MnMoO_4 \cdot H_2O$ (**2**)		$MnMoO_4 \cdot H_2O$ (**3**)		$Na_2Mn_2(MoO_4)_3 \cdot 3H_2O$	
d, Å	I/I_0, %	d, Å	I/I_0, %	d, Å	I/I_0, %	d, Å	I/I_0, %
6.810	13	5.086	4	5.581	23	7.948	100
5.609	38	4.754	23	4.700	100	5.183	3
5.471	15	4.382	11	4.386	3	4.766	4
4.733	93	4.032	3	3.967	5	4.718	6
4.635	17	3.823	13	3.805	3	4.517	9
3.978	20	3.320	100	3.789	5	4.368	8
3.794	15	3.234	23	3.408	14	4.206	20
3.421	100	3.213	11	3.374	5	3.549	16
3.389	42	2.982	5	3.326	63	3.465	9
3.243	15	2.921	9	3.234	6	3.447	28
2.885	25	2.885	5	2.876	27	3.169	70
2.840	30	2.665	8	2.833	13	3.113	10
2.814	32	2.547	3	2.804	10	3.090	10
2.755	12	2.484	5	2.738	3	2.805	20
2.747	15	2.289	2	2.695	3	2.683	8
2.698	8	2.207	3	2.664	6	2.601	4
2.411	7	2.194	4	2.484	3	2.295	6
2.368	9	2.079	6	2.402	3	2.269	10
2.359	8	2.075	5	2.369	3	2.014	6
2.231	4	2.071	4	2.356	3		
2.312	3	2.030	5				
2.276	8	2.026	3				

The position of the hydrogen atoms in $NaMn_2(OH)(H_2O)(MoO_4)_2$ were determined from a difference Fourier, but the positions and thermal parameters were not refined. The hydrogen positions in $MnMoO_4 \cdot H_2O$ were not found because of poorer crystal quality. This compound was obtained as twinned crystals that were so small that the twins could not be separated. Instead the crystal was aligned along a suspected zone axis and a matrix for the stronger reflections about this axis found. A data set for the aligned part of the crystal was collected, and all suspected twin reflections were rejected.[17]

Results

The results of the elemental analysis and TGA are shown in Table I. The three preparations carried out in acid or neutral solution (**1**–**3**) yielded products with a 1:1 ratio of Mn(II) to Mo(VI). The formula $MnMoO_4 \cdot H_2O$ requires a 7.74% weight loss resulting from water split out at elevated temperatures. The observed weight losses are indeed close to this value, with the poorest on (**2**) being lower by 0.6%. The X-ray powder patterns of the preparations are given in Table II as a means of distinguishing them. It is seen that each of the solids has a distinct pattern different from the others. Heating the monohydrates to 550 °C converted all three solids to α-$MnMoO_4$, the compound whose structure was described by Abrahams and Reddy.[10] It is therefore apparent that by variation of the pH of preparation it is possible to produce three different compounds of composition $MnMoO_4 \cdot H_2O$.

IR spectra for the three monohydrates are given in Table III. These spectra are characterized by a split peak in the OH stretching region, indicating somewhat different environments for the two water protons, and a band at 1610–1618 cm^{-1} for the water bend. There are a number of intense absorption bands in the region between 700 and 940 cm^{-1}. Two of them are characteristic of tetrahedral MoO_4 groups[18] while three more should result from octahedral MnO_6 groups. It is seen that the three monohydrates contain several bands in this region, but some are broad and not resolved. The bands near 940 cm^{-1} represent symmetric MoO_4 stretching while those near 840 and perhaps 720–760 cm^{-1} are

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(17) The structure of $MnMoO_4 \cdot H_2O$ was determined by Dr. J. M. Troup of Molecular Structure Corp., College Station, TX.

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Table III. Infrared Bands (cm^{-1}) for Manganese Molybdates[a]

$MnMoO_4 \cdot H_2O$				
pH ~7 (1)	pH ~4 (2)	pH ~5.5 (3)	α-$MnMoO_4$	$Na_2Mn_2(MoO_4)_3 \cdot 3H_2O$ (4)
3470 (m)	3480 (m)	3470 (m)	940 (s)	3510 (s)
3430 (m)	3420 (m)	3435 (m)	923 (s)	3395 (s)
1618 (s)	1610 (s)	1618 (m)	910 (s)	3235 (s)
938 (s)	922 (s)	932 (m)	866 (s)	1648 (m)
895 (s)	865 (s)	835 (m)	794 (s)	950 (s)
835 (s)	845 (s)	790 (m)	720 (s)	915 (s)
792 (s)	820 (s)	600 (w)	398 (a)	890 (s)
595 (m)	762 (s)	408 (w)	352 (w)	870 (s)
405 (m)	668 (vw)	335 (vw)	340 (m)	804 (s)
345 (w)	650 (vw)	290 (w)	300 (w)	718 (s)
288 (m)	548 (vw)			570 (m)
	435 (vw)			540 (m)
	410 (vw)			395 (m)
	350 (vw)			352 (m)
	326 (w)			290 (s)
	300 (vw)			
	285 (vw)			

[a] Intensities: s = strong, m = medium, w = weak, vw = very weak.

Table IV. Crystallographic Data for Manganese Molybdates

	$NaMn_2OH(H_2O)(MoO_4)_2$	$MnMoO_4$	$MnMoO_4 \cdot H_2O$
fw	487.76	214.88	232.90
cryst dimens, mm	0.077 × 0.07 × 0.084	0.14 × 0.13 × 0.03	0.05 × 0.10 × 0.15
space group	$C2/m$ (12)	$P2/c$ (13)	$P\bar{1}$ (2)
syst abs	hkl: $h + k = 2n + 1$	$h0l$: $l = 2n + 1$	none
cell parameters			
a, Å	9.534 (1)	4.818 (1)	5.776 (4)
b, Å	6.528 (1)	5.759 (1)	5.964 (4)
c, Å	7.715 (1)	4.965 (1)	6.992 (4)
α, deg	90.0	90.0	100.32 (5)
β, deg	115.83 (1)	90.82 (1)	95.56 (5)
γ, deg	90.0	90.0	106.81 (5)
V, $Å^3$	432.2 (2)	137.7 (1)	224.0 (1)
Z	2	2	2
d_{calcd}, g/cm^3	3.75	5.18	3.42
μ, cm^{-1}	58.55	90.45	55.90
no. of reflecns			
total	1413	985	2914
unique, $I > 3\sigma$	1203	729	1230
standards	$2,\bar{2},3$; $\bar{1},\bar{1},3$; $\bar{3},1,\bar{1}$	$\bar{2},\bar{2},\bar{1}$; $2,0,\bar{2}$; $2,\bar{2},\bar{1}$	1,1,0; 1,1,1; $1,1,\bar{1}$
R^a	0.025	0.039	0.070
$R_w{}^b$	0.035	0.049	0.078

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = (1/\sigma)(|F_o|^2)$.

for asymmetric stretching.[19] It will be shown later that the monohydrate prepared in neutral solution does indeed contain tetrahedral molybdate ions, as does α-$MnMoO_4$.

$Na_2Mn_2(MoO_4)_3 \cdot 3H_2O$. This compound formed under alkaline conditions and contained equal parts sodium and manganese but a 3:2 ratio of Mo to these elements. The compound lost a total of 7.8% H_2O, half being lost at 200 °C and the remainder at slightly above 300 °C. Its infrared spectrum is given in Table III. The large number of bands in the 700–950-cm^{-1} region may indicate two different site symmetries for the MoO_4 group. Thus, on the basis of the analytical results and the IR spectrum the compound is formulated as $Na_2Mn_2(MoO_4)_3 \cdot 3H_2O$.

None of the compounds crystallized from aqueous solution and described above correspond to those reported by others.[6,7,11,12] We, therefore, collected the yellow precipitate that formed in the early stages of the refluxing procedure. This yellow precipitate was indeed identified from its X-ray pattern as the product obtained by Corbet and Eyraud.[6] The precipitate recovered from neutral solution gave a weak X-ray pattern with only six reflections, indicating a poorly crystalline material. However, the yellow precipitate recovered from acid solutions was better crystallized and gave the full X-ray pattern reported earlier by other workers.[6,7] Thus, the initial yellow precipitate is yet another monohydrate but transforms into the three reported here at different pH values.

Table V. Positional and Thermal Parameters and Their Estimated Standard Deviations

atom	x	y	z	B_{eqv}, $Å^2$
		A. $NaMn_2OH(H_2O)(MoO_4)_2$		
Mo	0.08523 (2)	0.0000 (0)	0.29393 (3)	0.671 (3)
Mn	0.2500 (0)	0.2500 (0)	0.0000 (0)	0.842 (6)
Na	0.0000 (0)	0.5000 (0)	0.5000 (0)	1.70 (4)
O1	0.2391 (3)	0.0000 (0)	0.5215 (3)	1.51 (4)
O2	0.4684 (2)	0.2801 (3)	0.2638 (2)	1.09 (2)
O3	0.1712 (2)	0.0000 (0)	0.1251 (3)	1.12 (3)
O4	0.3548 (2)	0.0000 (0)	0.9157 (3)	0.097 (3)
H1	0.3047 (0)	0.0000 (0)	0.7910 (0)	5.0000 (0)
H2	0.5000 (0)	0.0820 (0)	0.0000 (0)	2.5000 (0)
		B. $MnMoO_4 \cdot H_2O$		
Mo	0.2435 (2)	0.3808 (2)	0.2519 (1)	1.36 (1)
Mn	0.1377 (3)	0.2124 (3)	0.7002 (2)	1.47 (3)
O1	0.128 (1)	0.145 (1)	0.378 (1)	1.7 (1)
O2	0.147 (1)	0.628 (1)	0.337 (1)	2.2 (2)
O3	0.563 (1)	0.471 (1)	0.287 (1)	2.1 (2)
O4	0.131 (2)	0.273 (2)	0.007 (1)	2.6 (2)
O5	0.410 (2)	0.021 (2)	0.730 (2)	3.5 (2)
		C. $MnMoO_4$		
Mo	0.5000 (0)	0.31448 (8)	0.7500 (0)	0.597 (5)
Mn	0.0000 (0)	0.1918 (2)	0.2500 (0)	0.85 (1)
O1	0.2505 (6)	0.1246 (5)	0.6046 (6)	0.88 (4)
O2	0.2875 (6)	0.3972 (5)	0.0527 (6)	0.84 (4)

Table VI. Bond Distances (Å) for $MnMoO_4 \cdot H_2O$

atom 1	atom 2	dist	atom 1	atom 2	dist
Mo	O1	1.796 (6)	Mn	O1′	2.172 (6)
Mo	O2	1.754 (7)	Mn	O2	2.139 (6)
Mo	O3	1.746 (6)	Mn	O3	2.142 (6)
Mo	O4	1.708 (7)	Mn	O4	2.117 (7)
Mn	O1	2.208 (6)	Mn	O5	2.210 (8)

Table VII. Bond Distances (Å) for $MnMoO_4$

atom 1	atom 2	dist	atom 1	atom 2	dist
Mo	O1	1.771 (3)	Mn	O1	2.155 (3)
Mo	O2	1.891 (3)	Mn	O1′	2.307 (3)
Mo	O2′	2.176 (3)	Mn	O2	2.078 (3)
O2	O2	2.428 (5)			

Crystal Structures. Single crystals of three of the molybdates were prepared. The brown phase $MnMoO_4 \cdot H_2O$ (**1**) was obtained by refluxing the original precipitate in the nearly neutral mother liquor. The same phase was obtained as a byproduct in the preparation of $Na_2Mn_2(MoO_4)_3 \cdot 3H_2O$. Hydrothermal treatment of this latter phase at 200 °C and pressures of ~100 atm for 3 days yielded anhydrous $MnMoO_4$ crystals while if the length of time was reduced to 1 day, single crystals of $NaMn_2(OH)(H_2O)(MoO_4)_2$ were obtained. Crystallographic data for each of these phases are collected in Table IV while positional and thermal parameters are given in Table V. The cell parameters for $MnMoO_4$ are within 3 standard deviations of those given earlier by Sleight and Chamberland.[14] Single crystals of the monohydrates **2** and **3** were not obtained. However, we will attempt to determine their structures by powder X-ray methods.[20]

$MnMoO_4 \cdot H_2O$ (1). This phase consists of molybdate tetrahedra and manganese–oxygen octahedra as shown in Figure 1. Bond distances are given in Table VI. The tetrahedra share corners with four different octahedra. Along the a direction the shared atoms are O2 and O3, along the b direction O1 and O2, and in

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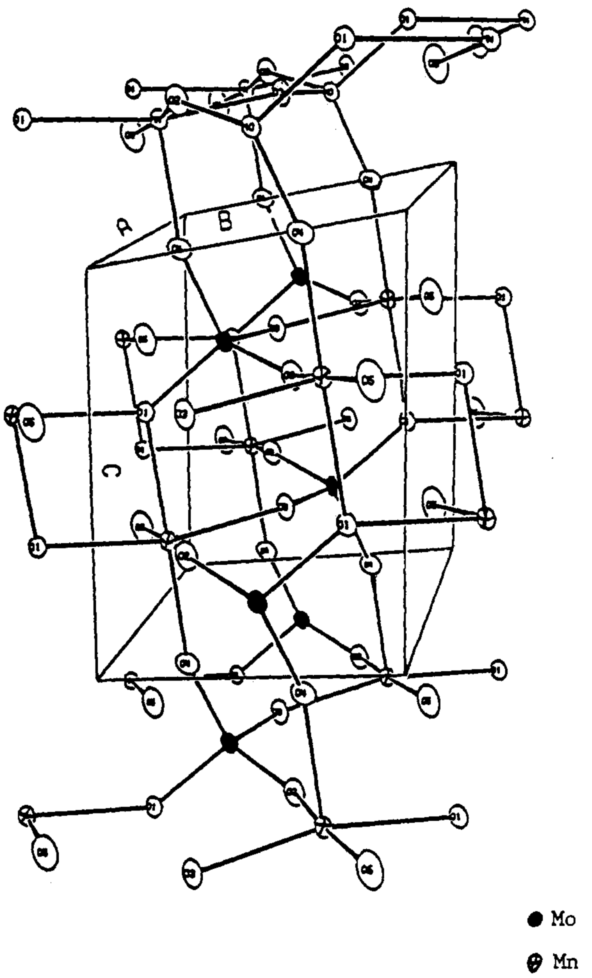

Figure 1. ORTEP drawing for $MnMoO_4 \cdot H_2O$ (**1**) showing the arrangement of the unit cell.

the *c* direction O1 and O4. The manganese atoms arranged about the center of symmetry at 0, 0, $^1/_2$ share an O1–O1 edge. This makes O1 three-coordinate, bonding to two Mn and one Mo atom. These metal–oxygen bonds are the longest except for Mn–O5. O5 is not shared, and this fact plus the longer distance from the metal indicate that it represents coordinately bound water.

$MnMoO_4$. This phase obtained at high pressure is isostructural with $NiWO_4$[15] as had been predicted.[14] Bond distances appear in Table VII. Both the molybdenum and manganese atoms are octahedrally coordinated. Each octahedron has two short, two medium, and two long metal–oxygen bonds. The metals sit on special positions while the oxygens are on general positions. Thus, only two unique oxygen atoms need be located. Octahedra of like metals are edge shared whereas unlike metal octahedra corner share. This requires three-coordination for each oxygen atom. The octahedra are highly distorted with angles ranging from 72.9 (1) to 101.7 (1)° in the molybdenum-containing octahedron and 75.7 (1) to 110.6 (2)° in the manganese one.

$NaMn_2(OH)(H_2O)(MoO_4)_2$. This phase was prepared by hydrothermal treatment of $Na_2Mn_2(MoO_4)_3 \cdot 3H_2O$ in 2 M sodium molybdate at 200 °C for 24 h. It is isostructural with the sodium zinc molybdate previously reported.[8] In the previous study, however, the hydrogen atoms were not located. Since the manganese crystals were of better quality, as evidenced by the greater amount of data obtained and the lower *R* factors, the structure was solved and we accomplished the purpose of fixing the position of the H atoms. Bond distances are shown in Table VIII. The esd's are considerably lower than for the corresponding zinc compound. A difference Fourier clearly showed a peak (H1) of about 1 e/Å^3 at a reasonable hydrogen distance (0.9 Å) from O4. Only O1 and O4 are two-coordinate, the other oxygen atoms being three-coordinate. Furthermore, the O1–O4 and O4–O4 distances are such as to indicate that hydrogen bonding between them is likely. Bonding a proton to O4 converts it to an OH group and makes the Mn–Mn bridging of the oxo–hydroxo type. H1 is 1.892 (3) Å away from O1, and thus hydrogen bonds to it with an O4–H1–O1 angle of 167.6 (1)°. The only other reasonable position for a hydrogen atom was near O4 at a special position, $^1/_2$, *y*, 0. This position contributes four hydrogens to the unit cell, which is two too many. The peak should be on the center of symmetry at $^1/_2$, 0, 0. However, as described earlier,[8] attempts to place the hydrogen there were unsuccessful. Instead, a split peak about the center was obtained. We interpret this as a half-weighted hydrogen statistically distributed about O4. Thus half the bridging O4 atoms are hydroxyl and the other half become water molecules. The Mn–Mn bridging sequence is then MnO(OH)MnO(H_2O)Mn... etc. Of the remaining residual electron density, the highest peaks (~0.5 e/Å^3) were too close to the metal atoms to be considered as H atoms.[21]

Table VIII. Bond Distances (Å) for $NaMn_2(OH)(H_2O)(MoO_4)_2$

atom 1	atom 2	dist	atom 1	atom 2	dist
Mo	O1	1.729 (3)	Mn	O2	2.196 (2)
Mo	O2	1.769 (2)[a]	Mn	O3	2.189 (1)
Mo	O3	1.816 (2)	Mn	O4	2.157 (1)
O4	H1	0.868 (2)	O4	H2	1.357 (2)
Na	O1	2.564 (3)[a]	Na	O2	2.505 (2)[b]

[a] Two times. [b] Four times.

Discussion

The results described here help to clarify certain discrepancies reported for molybdates of the latter half of the first-row transition metals. These discrepancies in large measure stem from the fact that the initial precipitate obtained on addition of the metal salt to sodium molybdate (at least in the case of Mn(II), Co(II), and Zn(II)) readily transforms to other monohydrates on refluxing. In the present case three such monohydrates were obtained (in addition to the initial monohydrate precipitates described by Pezerat[7,22]). Thus, if one is not careful, mixtures of these compounds may be obtained. Heating such a mixture should yield α-$MnMoO_4$, as all of the monohydrates form this phase at elevated temperatures. This is the compound used by Trifiro et al. in their catalytic studies[3,12] as shown by X-ray powder and infrared data on their preparation. However, the compound prepared by Sinhamahapatra and Bhattacharyya using ammonium molybdate as precipitant is apparently a phase other than the ones described in this paper. In fact, when they heated their compound, it did not yield α-$MnMoO_4$. Therefore, claims as to selectivity and reactivity orders for reactions catalyzed by transition-metal molybdates prepared under different conditions need to be treated with caution.

Supplementary Material Available: Tables of anisotropic temperature factors, bond angles, and observed and calculated structure factors for each structure (21 pages). Ordering information is given on any current masthead page.

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