Crystal Structure and Raman Spectroscopy of $FeVMoO_7$ and $CrVMoO_7$ with Mo═O Double Bonds

Xiandong Wang, Kevin R. Heier, Charlotte L. Stern, and Kenneth R. Poeppelmeier*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received January 28, 1998

Single crystals of $FeVMoO_7$ and $CrVMoO_7$ were grown by a flux method from $Fe_2O_3-V_2O_5-MoO_3$ and $Cr_2O_3-V_2O_5-MoO_3$ melts, respectively. Single-crystal X-ray diffraction revealed that $FeVMoO_7$ and $CrVMoO_7$ are isostructural, in which V^{5+} and Mo^{6+} ions in the $[VMoO_7]^{3-}$ units are crystallographically distinct, and one type of oxygen is bonded only to molybdenum, forming a Mo═O double bond. These rare structural features were also studied by infrared and Raman spectroscopy. Raman Mo═O stretching frequencies are consistent with the assignments made in previous surface studies of molybdate catalysts. Crystal data for $FeVMoO_7$: triclinic, space group $P\bar{1}$ (No. 2), with $a = 5.564(1)$ Å, $b = 6.669(1)$ Å, $c = 7.909(1)$ Å, $\alpha = 97.65(1)°$, $\beta = 90.33(1)°$, $\gamma = 101.32(2)°$ and $Z = 2$. Crystal data for $CrVMoO_7$: triclinic, space group $P\bar{1}$ (No. 2), with $a = 5.5273(9)$ Å, $b = 6.582(1)$ Å, $c = 7.8650(9)$ Å, $\alpha = 96.19(1)°$, $\beta = 89.87(1)°$, $\gamma = 102.01(1)°$, and $Z = 2$.

Introduction

Multicomponent vanadates/molybdates are widely used as catalysts for selective oxidation of hydrocarbons. The activity and selectivity of catalytic reactions for the desired products are significantly related to the structures of the catalysts used.[1−3] The focus of our research is to explore new and interesting vanadates/molybdates and to understand their remarkable solid-state chemistry. Our previous work on the $MO-V_2O_5-MoO_3$ ($M = Mg^{2+}$, Zn^{2+}, and Mn^{2+}) systems[4] revealed a new family of materials with the general formula $M_{2.5}VMoO_8$. Their structural features have been studied by X-ray single-crystal diffraction[4] and neutron powder diffraction.[5] $Mg_{2.5}VMoO_8$ showed good selectivity for the oxidative dehydrogenation of butane,[6] and $Mn_{2.5}VMoO_8$ and $Zn_{2.5}VMoO_8$ are likely to have similar properties.

As a continuation of this work, the $M_2O_3-V_2O_5-MoO_3$ ($M = Fe^{3+}$, Cr^{3+}) systems were selected to search for new and interesting ternary compounds which can incorporate trivalent transition metal ions. It was known that the binary compound ferric molybdate $Fe_2Mo_3O_{12}$, in the $Fe_2O_3-MoO_3$ system is a good catalyst for the oxidation of methanol to formaldehyde,[7] and it is also an important component in the Bi−Fe−Mo−O catalysts for selective ammoxidation of propane to acrylonitrile.[8] Therefore, new ternary compounds in the $M_2O_3-V_2O_5-MoO_3$ system should be interesting in selective oxidation. Although $FeVMoO_7$[9] and $CrVMoO_7$[10] were reported previously, the former was investigated only by powder X-ray diffraction,[11] and the latter has not been characterized at all. In this work the structures of $FeVMoO_7$ and $CrVMoO_7$ were investigated by X-ray single-crystal diffraction and by infrared and Raman spectroscopy.

Experimental Section

Synthesis. Polycrystalline $FeVMoO_7$ and $CrVMoO_7$ were prepared by the solid-state reaction of Fe_2O_3 (99+%, Aldrich), Cr_2O_3 (99.995%, Aldrich), V_2O_5 (99.6+%, Aldrich), and MoO_3 (99.5+%, Aldrich). Prior to calcination, appropriate amounts of mixed oxides were ground in an agate mortar and packed in alumina boats. The $FeVMoO_7$ sample was calcined at 650 °C for 35 h and then ground into powder and pressed into pellets. The pellets were further heated at 660 °C for 24 h and finally quenched to room temperature in air. The $CrVMoO_7$ sample was prepared in a similar way except with different calcination (670 °C for 48 h) and further heat treatment (800 °C for 48 h) conditions. The products were both single phase, as determined by powder X-ray diffraction. Differential thermal analysis (DTA) determined that $FeVMoO_7$ melts incongruently at 722(2) °C and $CrVMoO_7$ melts at 865(2) °C.

$FeVMoO_7$ and $CrVMoO_7$ single crystals were grown by a flux method in platinum crucibles. The composition of the melt, the heating

---

* Corresponding author. E-mail: krp@nwu.edu. Fax: (847) 491-7713.

(1) Brazdil, J. F.; Teller, R. G.; Grasselli, R. K.; Kostiner, E. In *Solid State Chemistry in Catalysis*; Grasselli, R. K., Brazdil, J. F., Eds.; (ACS Symposium Series 279); American Chemical Society: Washington, DC, 1985; pp 57−74.

(2) (a) Germain, J. E. In *Adsorption and Catalysis on Oxide Surfaces Studies in Surface Science and Catalysis 21*; Che, M., Bond, G. C., Eds.; Elsevier: New York, 1985; pp 355−368. (b) Grasselli, R. K. pp 275−285.

(3) (a) Moro-oka, Y.; He, D. H.; Ueda, W. In Adsorption and Catalysis on Oxide Surfaces; Che, M., Bond, G. C., Eds.; Elsevier: New York, 1985; pp 57−66. (b) Portela, M. F.; Pinheiro, C.; Dias, C.; Pires, M. J. *ibid*; pp 77−85.

(4) (a) $Mg_{2.5}VMoO_8$, Wang, X. D.; Stern, C. L.; Poeppelmeier, K. R. *J. Alloys Compd.* **1996**, *243*, 51−58. (b) $Zn_{2.5}VMoO_8$, Wang, X. D.; Heier, K. R.; Stern, C. L.; Poeppelmeier, K. R. *J. Alloys Compd.* **1997**, *255*, 190−194. (c) $Mn_{2.5}VMoO_8$, Wang, X. D.; Heier, K. R.; Stern, C. L.; Poeppelmeier, K. R. *J. Alloys Compd.* **1998**, *267*, 79−85.

(5) Wang, X. D.; Hu, Z. B.; Poeppelmeier, K. R.; Jogensen, J. D., in preparation.

(6) Harding, W. D.; Kung, H. H.; Kozhevnikov, V. L.; Poeppelmeier, K. R. *J. Catal.* **1993**, *144*, 597−610.

(7) Kung, H. H. *Transition Metal Oxides: Surface Chemistry and Catalysis*; Elsevier: Amsterdam, 1989; pp 218−221.

(8) (a) Jeitschko, W.; Sleight, A. W.; McClellan, W. R.; Weiher, J. F. *Acta Crystallogr.* **1976**, *B32*, 1163−1170. (b) Kim, Y. C.; Ueda, W.; Moro-Oka, Y. *Appl. Catal.* **1991**, *70*, 175−187. (c) Kim, Y. C.; Ueda, W.; Moro-Oka, Y. *Chem. Lett.* **1989**, 2173−2176.

(9) (a) Walczak, J.; Kurzawa, M.; Filipek, E. *J. Therm. Anal.* **1986**, *31*, 271−277. (b) Walczak, J.; Ziolkowski, J.; Kurzawa, M.; Treseniowska, L. *Pol. J. Chem.* **1985**, *59*, 713−719. (c) Walczak, J.; Kurzawa, M. *J. Therm. Anal.* **1988**, *34*, 679−684. (d) Walczak, J.; Kurzawa, M. *J. Therm. Anal.* **1986**, *31*, 531−538. (e) Walczak, J.; Kurzawa, M.; Tabero, P. *Thermochim. Acta* **1987**, *118*, 1−7.

(10) Walczak, J.; Filipek, E. *J. Therm. Anal.* **1990**, *36*, 2169−2172.

(11) Lebail, A.; Permer, L.; Laligant, Y. *Eur. J. Solid State Inorg. Chem.* **1995**, *32*, 883−892.

S0020-1669(98)00100-1 CCC: $15.00

Table 1. Crystal Growth Parameters for $FeVMoO_7$ and $CrVMoO_7$

crystal	composition	heating (°C h^{-1})	T_{max} (°C)[a]	cooling (°C h^{-1})	cooling range (°C)	weight loss (%)
$FeVMoO_7$	1.756 g of Fe_2O_3 2.000 g of V_2O_5 2.110 g of MoO_3	120	900	6	900−650	6.0
$CrVMoO_7$	2.024 g of Cr_2O_3 2.421 g of V_2O_5 2.555 g of MoO_3	120	900	5	900−650	8.7

[a] Soak time one hour.

Table 2. Crystallographic Data for $FeVMoO_7$ and $CrVMoO_7$

chemical formula	$FeVMoO_7$	$CrVMoO_7$
fw	314.72	310.87
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No.2)
a, Å	5.564(1)	5.5273(9)
b, Å	6.669(1)	6.582(1)
c, Å	7.909(1)	7.8650(9)
α, deg	96.29(1)	96.19(1)
β, deg	90.33(1)	89.87(1)
γ, deg	101.32(2)	102.01(1)
V, Å^3	285.92(8)	278.18(7)
Z	2	2
T, °C	−120	−120
λ, Å	0.710 69	0.710 69
ρ_{calc}, g/cm^3	3.655	3.711
μ, mm^{-1}	6.231	5.753
R^a	0.031	0.032
R_wb	0.050	0.048

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

Table 3. Positional Parameters and Equivalent Isotropic Displacement Coefficients [Å^2][a] for $FeVMoO_7$ and $CrVMoO_7$

atom	x	y	z	U(eq)
Fe	−0.1712(1)	0.3093(1)	−0.59662(8)	0.0049(1)
V	0.3112(1)	0.2427(1)	−0.33417(8)	0.0026(2)
Mo	0.29607(7)	0.21076(6)	0.10859(4)	0.0061(1)
O(1)	0.2074(7)	−0.0064(5)	−0.3903(4)	0.0097(7)
O(2)	0.1092(6)	0.3768(5)	−0.4251(4)	0.0055(7)
O(3)	0.3341(6)	0.2958(6)	−0.1066(4)	0.0095(7)
O(4)	0.5863(6)	0.3084(5)	−0.4127(4)	0.0090(7)
O(5)	0.0628(6)	0.3096(6)	0.2155(4)	0.0092(7)
O(6)	0.5681(6)	0.2982(6)	0.2349(4)	0.0119(8)
O(7)	0.2294(8)	−0.0487(6)	0.0969(5)	0.0180(9)
Cr	−0.1677(1)	0.3142(1)	−0.5964(1)	0.0034(2)
V	0.3111(1)	0.2416(1)	−0.3346(1)	0.0020(2)
Mo	0.29824(7)	0.21107(6)	0.11031(5)	0.0056(1)
O(1)	0.2057(6)	−0.0113(5)	−0.3889(5)	0.0079(8)
O(2)	0.1052(6)	0.3764(5)	−0.4238(4)	0.0040(7)
O(3)	0.3394(6)	0.2967(6)	−0.1066(5)	0.0085(8)
O(4)	0.5891(6)	0.3114(5)	−0.4168(5)	0.0070(7)
O(5)	0.0686(6)	0.3164(5)	0.2194(4)	0.0068(7)
O(6)	0.5745(6)	0.2932(6)	0.2344(5)	0.0092(8)
O(7)	0.2200(7)	−0.0528(6)	0.1005(6)	0.0156(9)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Bond Lengths (Å) and Their Corresponding Differences Δ (Fe−Cr, Å) for $FeVMoO_7$ and $CrVMoO_7$

$FeVMoO_7$		$CrVMoO_7$		Δ
Fe−O(1)	1.982(3)	Cr−O(1)	1.952(3)	0.030
Fe−O(2)	2.011(3)	Cr−O(2)	1.980(3)	0.031
Fe−O(2)	2.041(3)	Cr−O(2)	1.982(3)	0.059
Fe−O(4)	1.989(3)	Cr−O(4)	1.947(3)	0.042
Fe−O(5)	1.981(3)	Cr−O(5)	1.947(3)	0.034
Fe−O(6)	1.949(3)	Cr−O(6)	1.925(3)	0.024
V−O(1)	1.658(3)	V−O(1)	1.654(3)	0.004
V−O(2)	1.762(3)	V−O(2)	1.770(3)	−0.008
V−O(3)	1.795(3)	V−O(3)	1.791(4)	0.004
V−O(4)	1.652(3)	V−O(4)	1.660(3)	−0.008
Mo−O(3)	1.852(3)	Mo−O(3)	1.853(4)	−0.001
Mo−O(5)	1.750(3)	Mo−O(5)	1.750(3)	0.000
Mo−O(6)	1.771(3)	Mo−O(6)	1.768(3)	0.003
Mo−O(7)	1.689(4)	Mo−O(7)	1.694(4)	−0.005

history, and the weight loss are summarized in Table 1. After the slow cooling procedure, melts were further cooled to room temperature at about 60 °C h^{-1}. In this way, large (1−2 mm) yellow/orange bar-like $FeVMoO_7$ crystals and smaller (<1 mm) dark brown $CrVMoO_7$ crystals were produced. The approximate compositions of the crystals used for X-ray data collection were determined by EDAX to be Fe:V:Mo (atomic ratio) = 1.01:1.00:0.91 and Cr:V:Mo (atomic ratio) = 1.00:1.16:0.92. The weight loss during crystal growth is mainly due to the evaporation of vanadium oxide and molybdenum oxide.

Crystallographic Determination. Crystals were mounted on glass fibers for study by single-crystal X-ray diffraction, and data was collected on an Enraf-Nonius CAD-4 diffractometer. Relevant crystallographic data are listed in Table 2 and in more detail in the Supporting Information. Atomic positions and equivalent isotropic thermal parameters are presented in Table 3. All atoms were refined anisotropically. Selected bond lengths are compared in Table 4. The structures were solved by direct methods[12] and expanded using Fourier techniques.[13] All calculations were performed using the TEXSAN[14] software package. Population refinements revealed no indication of Mo/V disorder in either $FeVMoO_7$ or $CrVMoO_7$.

Spectroscopic and Magnetic Measurements. Mid-infrared (400−4400 cm^{-1}) spectra of polycrystalline $FeVMoO_7$ and $CrVMoO_7$ were collected using a Bio-Rad FTS-60 FTIR spectrophotometer at 2 cm^{-1} resolution. Raman (100−2000 cm^{-1}) spectra of polycrystalline $FeVMoO_7$ and $CrVMoO_7$ were collected on a Bio-Rad FT-Raman spectrophotometer with 4 cm^{-1} resolution (50 scans for $CrVMoO_7$, 500 scans for $FeVMoO_7$). Magnetic susceptibility data were collected on a Quantum Design SQUID susceptometer between 5 and 300 K. Polycrystalline samples were encased in sealed gelatin capsules and zero field cooled to 5 K. A 1 kG field was applied during measurements. The data were corrected for core diamagnetism.[15]

Results

Structure. Triclinic $FeVMoO_7$ and $CrVMoO_7$ are isostructural (Figure 1a) and closely related to monoclinic $MgMo_2O_7$ (Figure 1b).[16] The structures are composed of corner-shared tetrahedral anions $[A_2O_7]^{n-}$ (A_2 = V + Mo, $n = -3$; A_2 = Mo + Mo, $n = -2$) which coordinate to Fe^{3+}, Cr^{3+}, or Mg^{2+} to form isolated edge-shared M_2O_{10} octahedral dimers (M = Fe,

---

(12) Sheldrick, G. M. SHELXS86. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: London/New York, 1985; pp 175−189.

(13) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. In *The DIRDIF-94 Program System*; Technical Report of the Crystallography Laboratory; University of Nijmegen. The Netherlands, 1994.

(14) (a) *TEXSAN*: *Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1992. (b) Cromer, D. T.; Waber, J. T. Scattering Factors for Non-hydrogen Atoms. In *International Tables for X-ray Crystallography*; Kyroch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(15) Mulay, L. N. In *Magnetic Susceptibility*; John Wiley & Sons: New York, 1963; p 1782.

(16) Stadnicka, K.; Haber, J.; Kozlowski, R. *Acta Crystallogr.* **1977**, *B33*, 3859−3862.

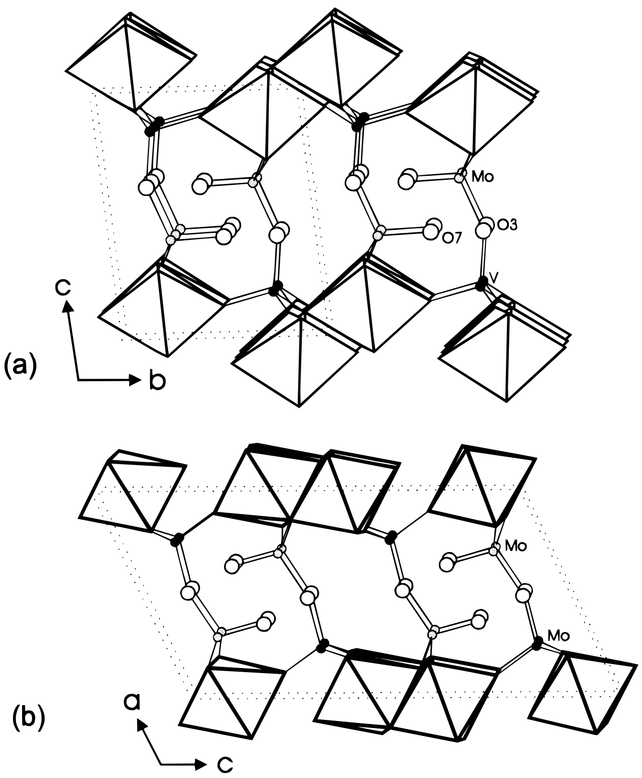

Figure 1. (a) Structure of $FeVMoO_7$ or $CrVMoO_7$: octahedra = FeO_6 or CrO_6. (b) Structure of $MgMo_2O_7$[16] (space group $P2_1/c$, $a = 8.111(2)$ Å, $b = 5.700(1)$ Å, $c = 15.002(3)$ Å, $\beta = 115.26(2)°$, $Z = 4$): octahedra = MgO_6.

Cr, or Mg). However, these similar structural units are arranged slightly differently in $MgMo_2O_7$, resulting in the different crystal structures (Figures 1 and 2). Despite the obvious similarities between the two structures, there is no simple transformation from one to the other.

In the $MVMoO_7$ structure, the M_2O_{10} octahedral dimers are bonded to the $[VMoO_7]^{3-}$ anions through five of the six terminal oxygens in each $[VMoO_7]^{3-}$ unit and are all aligned in the same direction (Figure 2a), in contrast to the herringbone pattern of the Mg_2O_{10} dimers in $MgMo_2O_7$ (Figure 2b). Fe−O bonds are on average 0.03 Å longer than equivalent Cr−O bonds (see Table 4), reflecting the difference in the effective ionic radii of high spin Fe^{3+} (0.645 Å) and Cr^{3+} (0.615 Å).[17]

In the *a* direction $[VMoO_7]^{3-}$ anions stack in columns. Adjacent columns are alternately face-to-face and back-to-back in terms of the Mo−O(7) bonds, similar to the arrangement of $[Mo_2O_7]^{2-}$ anions in $MgMo_2O_7$ (Figure 1). Despite the change from Fe^{3+} to Cr^{3+} in the two compounds, the $[VMoO_7]^{3-}$ groups remain virtually identical in terms of bond distances and angles (see Table 4). O(7) is only bonded to one molybdenum atom forming a Mo−oxo double bond with the shortest bond length in the MoO_4 tetrahedra (1.69 Å), while the next nearest O(7)-cation contact is more than 3.25 Å. The V/Mo bonds to the bridging O(3) are the longest in the corner-shared tetrahedral unit, which is consistent with previously investigated corner-shared poly-tetrahedral anions.[16,18] The relative orientation of the corner-shared VO_4−MoO_4 tetrahedra (Figure 3a) in $FeVMoO_7$ is illustrated by projecting atoms from V to Mo (Figure 3b). The $[VMoO_7]^{3-}$ groups adopt a nearly eclipsed conformation, similar to $[Mo_2O_7]^{2-}$ in $MgMo_2O_7$.

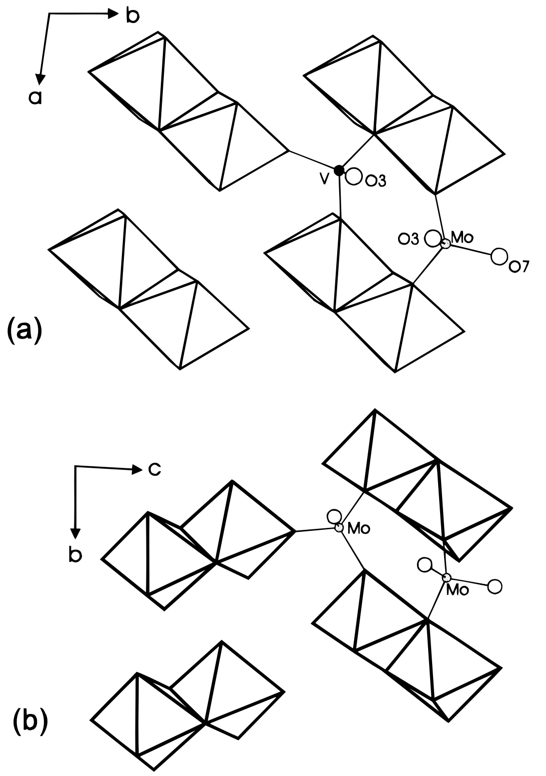

Figure 2. (a) Fe_2O_{10} octahedral dimers and their linkage to VO_4 and MoO_4 tetrahedra in $FeVMoO_7$ viewed approximately along the *c* axis; (b) Mg_2O_{10} octahedral dimers and their linkage to MoO_4 tetrahedra in $MgMo_2O_7$ viewed along the *a* axis. Open circles represent the bridging and Mo-oxo oxygens (pointing to right).

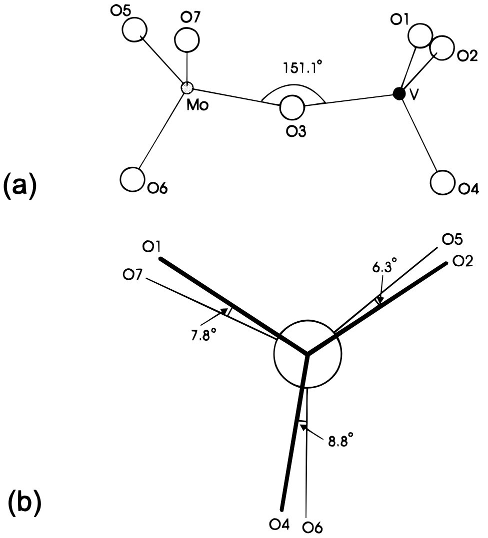

Figure 3. The geometry of $[VMoO_7]^{3-}$ units in $FeVMoO_7$: (a) V−O−Mo bridging; (b) projection from V to Mo, bridging oxygen is omitted.

The bond valences of molybdenum and vanadium were calculated[19] to be +5.94 and +5.12, respectively, in $FeVMoO_7$, and +5.92 and +5.09, respectively, in $CrVMoO_7$, indicating that Mo^{6+} and V^{5+} are ordered in the structure. These result are consistent with least-squares refinements on the populations of V and Mo and are in contrast to the complete disorder between V^{5+} and Mo^{6+} in $M_{2.5}VMoO_8$ (M = Mg^{2+}, Zn^{2+},

---

(17) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767.

(18) (a) Kato, K.; Takayama-Muromachi, E. *Acta Crystallogr.* **1985**, *C41*, 647−649. (b) Gatehouse, B. M.; Guddat, L. W.; Roth, R. S. *J. Solid State Chem.* **1987**, *71*, 390−395. (c) Lii, K. H.; Chen, Y. B.; Su, C. C.; Wang, S. L. *J. Solid State Chem.* **1989**, *82*, 156−160.

(19) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244−247.

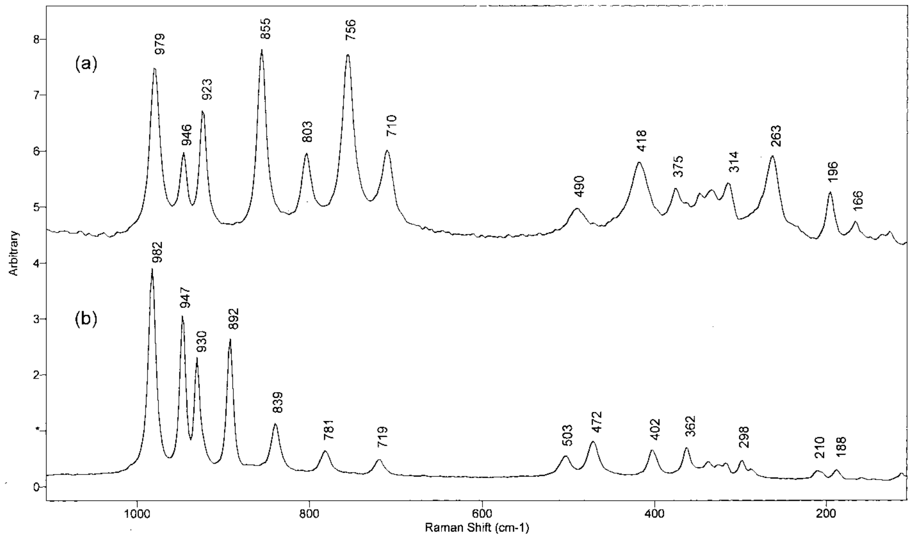

Figure 4. Raman spectra of polycrystalline (a) $FeVMoO_7$ and (b) $CrVMoO_7$.

Table 5. Observed Raman Bands (cm^{-1}) and IR Absorptions (cm^{-1}) for $FeVMoO_7$ and $CrVMoO_7$

Raman[a]		IR[a]		
(Fe)	(Cr)	(Fe)	(Cr)	assignment
979 s	982 s	975 m sh	978 m	Mo=O str
946 m	947 s	943 s	946 m	V/Mo−O str
923 s	930 s	889 s	903 m	
855 s	892 s	842 m sh	848 s br	
803 m	839 m	809 s br	800 m sh	
756 s	781 w			
710 m	719 w	698 m br	732 m br	V−O(3)−Mo
490 w	503 w	496 m	549 m	Fe/Cr−O str
418 m	472 w	458 m	472 w	

[a] s = strong, m = moderate, w = weak, br = broad, sh = shoulder.

Mn^{2+}).[4] Our results on the structure of $FeVMoO_7$ are in accordance with the results of the earlier powder X-ray diffraction study.[11] However, the standard uncertainties of the oxygen coordinates and interatomic distances have been significantly improved. The unreasonable bond valence (+7.1) for molybdenum obtained from the powder X-ray diffraction structure[11] is due to inaccurate Mo−O bond lengths.

IR and Raman Spectra. The IR spectrum of $FeVMoO_7$ is consistent with that previously reported[20] and is similar to that of $CrVMoO_7$. The Raman spectra of $FeVMoO_7$ and $CrVMoO_7$ are presented in Figure 4. The Raman shifts and IR absorptions are listed in Table 5. Assigments were made on the basis of comparisons of the title compounds with one another and with similar compounds.[21−23] The highest wavenumber Raman shifts (979 cm^{-1} for $FeVMoO_7$ and 982 cm^{-1} for $CrVMoO_7$) are assigned to the Mo=O(7) double bond stretch. Calculated Raman stretching frequencies for the Mo=O(7) bonds are 992 and 982 cm^{-1} for $FeVMoO_7$ and $CrVMoO_7$ respectively, and are consistent with the observed values according to the empirical equation[24]

$$\nu\ (\mathrm{cm}^{-1}) = 32895 \exp(-2.073R) \qquad (1)$$

where ν is the Mo−O stretching frequency, and R is the Mo−O bond distance. The Raman shifts of 710 cm^{-1} in $FeVMoO_7$ and 719 cm^{-1} in $CrVMoO_7$ are probably due to stretching of the bridging V−O(3)−Mo.[21]

The five remaining peaks above 700 cm^{-1} in each Raman spectrum are also assigned to Mo/V−O stretching vibrations. The crystallographic similarity of the $[VMoO_7]^{3-}$ anions in the two compounds is reflected in the similarity of the Raman spectra in this region. However, three of these peaks in $FeVMoO_7$ are shifted 25−35 cm^{-1} lower in energy. This shift to lower wavenumbers is probably due to the weaker iron−oxygen bonds associated with high spin Fe^{3+}. These less rigid bonds may in turn allow the Mo/V−O bonds to vibrate at a lower energy. The Raman peaks below 500 cm^{-1} are probably due to Fe/Cr−O stretching and various bending modes.

Magnetic Susceptibilities. Least-squares refinements of the reciprocal molar susceptibility versus temperature data ($1/\chi \approx T$) in the range 30−300 K for $FeVMoO_7$ and 60−300 K for $CrVMoO_7$ revealed a Curie−Weiss behavior. The calculated $\mu_{\mathrm{eff}} = 6.02\ \mu_B$ (spin-only 5.92 μ_B) for $FeVMoO_7$ indicates that the Fe^{3+} ions ($3d^5$) are in high-spin state. The calculated $\mu_{\mathrm{eff}} = 3.95\ \mu_B$ (spin-only 3.87 μ_B) for $CrVMoO_7$ indicates Cr^{3+} ions ($3d^3$). The negative Weiss constants ($\theta = -51$ K for $FeVMoO_7$ and $\theta = -63$ K for $CrVMoO_7$) reveal antiferromagnetic interactions between the M^{3+} ions at 16 K and 34 K for $FeVMoO_7$ and $CrVMoO_7$, respectively.

Discussion

The structures of $MVMoO_7$ (M = Fe^{3+}, Cr^{3+}) display some rare and interesting characteristics. The most unusual characteristic is the complete ordering of V^{5+} and Mo^{6+} on different crystallographic sites. Least-squares refinements on the populations of the two unique tetrahedral sites show there is no mixing of cations on either position. Bond-valence calculations also confirm the ordered model. To our knowledge, this is the first oxide in which this situtation is observed. Usually V^{5+} and Mo^{6+} are either completely disordered[4] or at least partially disordered.[25]

One consequence of the V^{5+}/Mo^{6+} ordering, and perhaps the most interesting feature of the structure, is the presence of one-

---

(20) (a) Kurzawa, M. *J. Mater. Sci. Lett.* **1992**, 976−979. (b) Iordanova, R.; Dimitriev, Y.; Dimitrov, V.; Klissurski, D. *J. Non-Cryst. Solids* **1994**, *167*, 74−80.

(21) (a) $Na_4V_2O_7$, Dupuis, T.; Viltange, M. *Mikrochim. Ichnoanal. Acta* **1963**, 232−238. (b) $Cu_{2-x}Mg_xV_2O_7$, de Waal, D.; Hutter, C. *Mater. Res. Bull.* **1994**, *29*, 843−849.

(22) Baran, E. J. *J. Mol. Struct.* **1978**, *48*, 441−443.

(23) Preudhomme, J.; Parte, P. *Spectrochim. Acta* **1971**, *27A*, 1817−1835.

(24) Hardcastle, F. D.; Wachs, I. E. *J. Raman Spectrosc.* **1990**, *21*, 683−691.

(25) Laligant, Y.; Permer, L.; Lebail, A. *Eur. J. Solid State Inorg. Chem.* **1995**, *32*, 325−334.

coordinate oxygen. Oxygen O(7) is only bonded to one molybdenum in the structure resulting in a Mo−oxo double bond. Although Mo−oxo double bonds are common in organometallic complexes,[26,27] they are extremely rare in solid-state oxides. $FeVMoO_7$, $CrVMoO_7$, and $MgMo_2O_7$ are the only three known complex oxides containing such Mo−oxo double bonds. The simple oxide α-MoO_3 also contains Mo−oxo double bonds,[28] but molybdenum is in the octahedral coordination instead of the tetrahedral.

By contrast, it is well-known that Mo−oxo double bonds on the *surface* of molybdate catalysts are common and play an important role in catalytic mechanisms. For example, in the proposed mechanism for the oxidation of methanol to formaldehyde on MoO_3,[29] methanol is adsorbed dissociatively on a dioxomolybdenum species, while abstraction of the hydrogen atom is accomplished by an adjacent dioxomolybdenum. Another example is the ammoxidation of propylene to acrylonitrile on the surface of α-$Bi_2Mo_3O_{12}$. A reaction mechanism has been proposed with active sites containing two Mo−dioxo groups bridged by Bi−O groups.[30]

Although no direct crystallographic evidence for terminal Mo−oxo double bonds formed on the surfaces of supported molybdate catalysts is available, they have been extensively characterized by Raman spectroscopy.[31] Therefore, in $MVMoO_7$ ($M = Fe^{3+}$, Cr^{3+}), the crystallographically observable Mo−oxo double bonds can serve as models for surface Raman studies. Using the observed Mo═O bond distances in $FeVMoO_7$ and $CrVMoO_7$ and the empirical eq 1, the expected Raman shifts can be predicted. These predicted values agree very well with the experimental values (Table 5) and fall within the range (950−1020 cm^{-1})[24] commonly assigned to Mo−oxo double bonds. These results provide an independent confirmation for the assignment of Mo−oxo surface double bonds.

Conclusion

The V/Mo ordering and one-coordinate oxygen in $FeVMoO_7$ and $CrVMoO_7$ allow for Raman studies of a well-characterized Mo−oxo double bond in a purely oxide environment. These unusual structural features make them good models of the surface oxygen coordination of molybdate catalysts.

Acknowledgment. The authors thank Dr. Larry Cirjak and acknowledge an Extramural Research Award (EMRA) from BP America, Inc., the National Science Foundation, Solid State Chemistry (award DMR-9412971), and the use of central facilities supported by the MRSEC program of the National Science Foundation (grant DMR-9632472) at the Materials Research Center of Northwestern University.

Supporting Information Available: Plots of the molar magnetic susceptibility and inverse susceptibility versus temperature for $FeVMoO_7$ and $CrVMoO_7$ (2 pages). Two X-ray crystallographic files, in CIF format, are available on the Internet. Ordering and access information is given on any current masthead page.

IC980100U

---

(26) Oku, H.; Ueyama, N.; Nakamura, A. *Inorg. Chem.* **1997**, *36*, 1504−1516.

(27) Vetter, W. M.; Sen, A. *Organometallics* **1991**, *10*, 244−250.

(28) Kihlborg, L. *Ark. Kemi* **1963**, *21*, 357−364.

(29) Allison, J. N.; Goddard, W. A., III *J. Catal.* **1985**, *92*, 127−135.

(30) Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. *J. Catal.* **1984**, *87*, 363−380.

(31) (a) Hardcastle, F. D.; Wachs, I. E. *J. Raman Spectrosc.* **1990**, *21*, 683−691. (b) Hu, H.; Wachs, I. E. *J. Phys. Chem.* **1995**, *99*, 10897−10922. (c) Ono, T.; Ogata, N.; Miyaryo, Y. *J. Catal.* **1996**, *161*, 78−86. (d) Plyuto, Yu. V.; Van Langeveld, A. D.; Babich, I. V.; Moulijn, J. A.; Plyuto, I. V. *Colloids Surf.* **1997**, *A125*, 225−230.