

Crystal Structure and Raman Spectroscopy of FeVMoO₇ and CrVMoO₇ with Mo=O Double Bonds

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Single crystals of FeVMoO₇ and CrVMoO₇ were grown by a flux method from Fe₂O₃–V₂O₅–MoO₃ and Cr₂O₃–V₂O₅–MoO₃ melts, respectively. Single-crystal X-ray diffraction revealed that FeVMoO₇ and CrVMoO₇ are isostructural, in which V⁵⁺ and Mo⁶⁺ ions in the [VMoO₇]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 FeVMoO₇: triclinic, space group *P* $\bar{1}$ (No. 2), with *a* = 5.564(1) Å, *b* = 6.669(1) Å, *c* = 7.909(1) Å, α = 97.65(1)°, β = 90.33(1)°, γ = 101.32(2)° and *Z* = 2. Crystal data for CrVMoO₇: triclinic, space group *P* $\bar{1}$ (No. 2), with *a* = 5.5273(9) Å, *b* = 6.582(1) Å, *c* = 7.8650(9) Å, α = 96.19(1)°, β = 89.87(1)°, γ = 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–V₂O₅–MoO₃ (M = Mg²⁺, Zn²⁺, and Mn²⁺) systems⁴ revealed a new family of materials with the general formula M_{2.5}VMoO₈. Their structural features have been studied by X-ray single-crystal diffraction⁴ and neutron powder diffraction.⁵ Mg_{2.5}VMoO₈ showed good selectivity for the oxidative dehydrogenation of butane,⁶ and Mn_{2.5}VMoO₈ and Zn_{2.5}VMoO₈ are likely to have similar properties.

As a continuation of this work, the M₂O₃–V₂O₅–MoO₃ (M = Fe³⁺, Cr³⁺) 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 Fe₂Mo₃O₁₂, in the Fe₂O₃–MoO₃ 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 M₂O₃–V₂O₅–MoO₃ system should be interesting in selective oxidation. Although FeVMoO₇⁹ and CrVMoO₇¹⁰ 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 FeVMoO₇ and CrVMoO₇ were investigated by X-ray single-crystal diffraction and by infrared and Raman spectroscopy.

Experimental Section

Synthesis. Polycrystalline FeVMoO₇ and CrVMoO₇ were prepared by the solid-state reaction of Fe₂O₃ (99+%, Aldrich), Cr₂O₃ (99.995%, Aldrich), V₂O₅ (99.6+%, Aldrich), and MoO₃ (99.5+%, Aldrich). Prior to calcination, appropriate amounts of mixed oxides were ground in an agate mortar and packed in alumina boats. The FeVMoO₇ 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 CrVMoO₇ 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 FeVMoO₇ melts incongruently at 722(2) °C and CrVMoO₇ melts at 865(2) °C.

FeVMoO₇ and CrVMoO₇ single crystals were grown by a flux method in platinum crucibles. The composition of the melt, the heating

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Table 1. Crystal Growth Parameters for FeVMoO₇ and CrVMoO₇

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 ₂ O ₃	120	900	6	900–650	6.0
	2.000 g of V ₂ O ₅					
	2.110 g of MoO ₃					
CrVMoO ₇	2.024 g of Cr ₂ O ₃	120	900	5	900–650	8.7
	2.421 g of V ₂ O ₅					
	2.555 g of MoO ₃					

^a Soak time one hour.**Table 2.** Crystallographic Data for FeVMoO₇ and CrVMoO₇

chemical formula	FeVMoO ₇	CrVMoO ₇
fw	314.72	310.87
space group	P1̄ (No. 2)	P1̄ (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 _w b	0.050	0.048

^a R = Σ||F_o – |F_c||/Σ|F_o|. ^b R_w = [Σw(|F_o – |F_c||)²/Σw|F_o|²]^{1/2}.

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 FeVMoO₇ crystals and smaller (<1 mm) dark brown CrVMoO₇ 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 methods¹² and expanded using Fourier techniques.¹³ All calculations were performed using the TEXSAN¹⁴ software package. Population refinements revealed no indication of Mo/V disorder in either FeVMoO₇ or CrVMoO₇.

Spectroscopic and Magnetic Measurements. Mid-infrared (400–4400 cm⁻¹) spectra of polycrystalline FeVMoO₇ and CrVMoO₇ were collected using a Bio-Rad FTS-60 FTIR spectrophotometer at 2 cm⁻¹ resolution. Raman (100–2000 cm⁻¹) spectra of polycrystalline FeVMoO₇ and CrVMoO₇ were collected on a Bio-Rad FT-Raman spectrophotometer with 4 cm⁻¹ resolution (50 scans for CrVMoO₇, 500 scans for FeVMoO₇). 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

Table 3. Positional Parameters and Equivalent Isotropic Displacement Coefficients [Å²]^a for FeVMoO₇ and CrVMoO₇

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 U_{ij} tensor.**Table 4.** Selected Bond Lengths (Å) and Their Corresponding Differences Δ (Fe–Cr, Å) for FeVMoO₇ and CrVMoO₇

	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

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 FeVMoO₇ and CrVMoO₇ are isostructural (Figure 1a) and closely related to monoclinic MgMo₂O₇ (Figure 1b).¹⁶ The structures are composed of corner-shared tetrahedral anions [A₂O₇]ⁿ⁻ (A₂ = V + Mo, n = –3; A₂ = Mo + Mo, n = –2) which coordinate to Fe³⁺, Cr³⁺, or Mg²⁺ to form isolated edge-shared M₂O₁₀ octahedral dimers (M = Fe,

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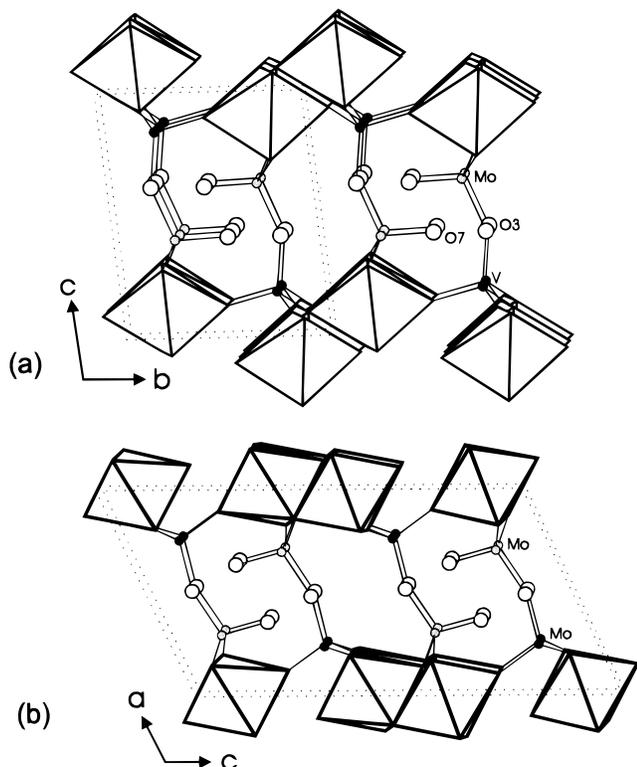


Figure 1. (a) Structure of FeVMoO₇ or CrVMoO₇: octahedra = FeO₆ or CrO₆. (b) Structure of MgMo₂O₇¹⁶ (space group *P2₁/c*, *a* = 8.111(2) Å, *b* = 5.700(1) Å, *c* = 15.002(3) Å, β = 115.26(2)°, *Z* = 4): octahedra = MgO₆.

Cr, or Mg). However, these similar structural units are arranged slightly differently in MgMo₂O₇, 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 MVMoO₇ structure, the M₂O₁₀ octahedral dimers are bonded to the [VMoO₇]³⁻ anions through five of the six terminal oxygens in each [VMoO₇]³⁻ unit and are all aligned in the same direction (Figure 2a), in contrast to the herringbone pattern of the Mg₂O₁₀ dimers in MgMo₂O₇ (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 Fe³⁺ (0.645 Å) and Cr³⁺ (0.615 Å).¹⁷

In the *a* direction [VMoO₇]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 [Mo₂O₇]²⁻ anions in MgMo₂O₇ (Figure 1). Despite the change from Fe³⁺ to Cr³⁺ in the two compounds, the [VMoO₇]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 MoO₄ 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 VO₄—MoO₄ tetrahedra (Figure 3a) in FeVMoO₇ is illustrated by projecting atoms from V to Mo (Figure

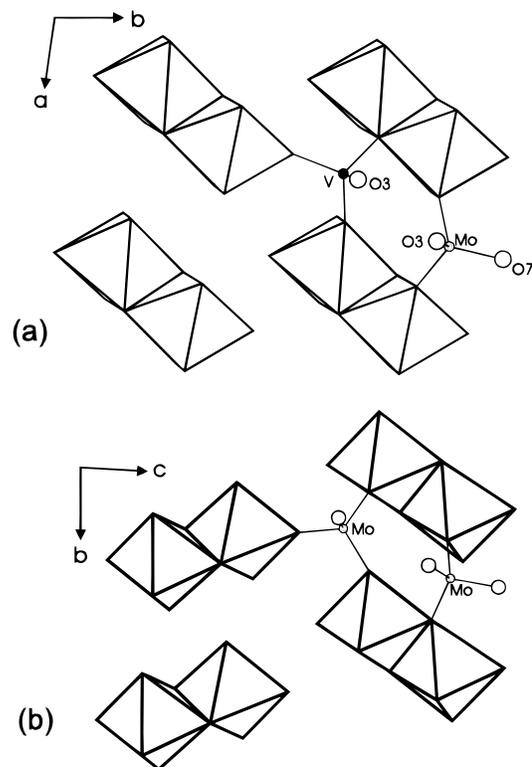


Figure 2. (a) Fe₂O₁₀ octahedral dimers and their linkage to VO₄ and MoO₄ tetrahedra in FeVMoO₇ viewed approximately along the *c* axis; (b) Mg₂O₁₀ octahedral dimers and their linkage to MoO₄ tetrahedra in MgMo₂O₇ viewed along the *a* axis. Open circles represent the bridging and Mo-oxo oxygens (pointing to right).

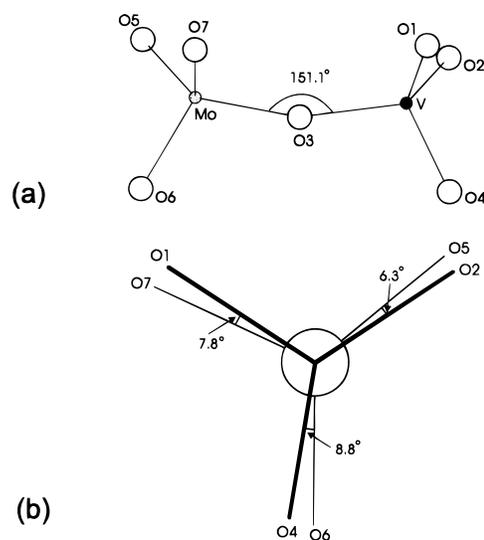


Figure 3. The geometry of [VMoO₇]³⁻ units in FeVMoO₇: (a) V—O—Mo bridging; (b) projection from V to Mo, bridging oxygen is omitted.

3b). The [VMoO₇]³⁻ groups adopt a nearly eclipsed conformation, similar to [Mo₂O₇]²⁻ in MgMo₂O₇.

The bond valences of molybdenum and vanadium were calculated¹⁹ to be +5.94 and +5.12, respectively, in FeVMoO₇, and +5.92 and +5.09, respectively, in CrVMoO₇, indicating that Mo⁶⁺ and V⁵⁺ 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 V⁵⁺ and Mo⁶⁺ in M_{2.5}VMoO₈ (M = Mg²⁺, Zn²⁺,

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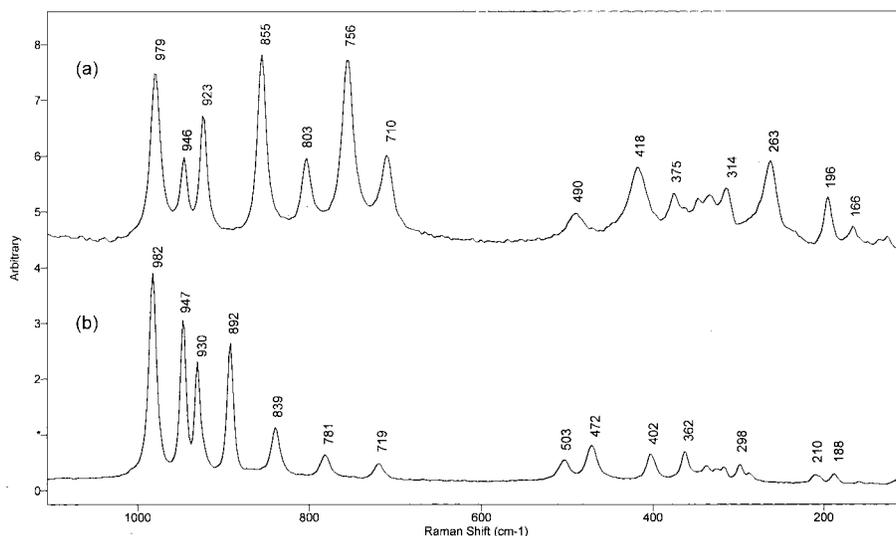


Figure 4. Raman spectra of polycrystalline (a) FeVMoO₇ and (b) CrVMoO₇.

Table 5. Observed Raman Bands (cm⁻¹) and IR Absorptions (cm⁻¹) for FeVMoO₇ and CrVMoO₇

Raman ^a		IR ^a		assignment
(Fe)	(Cr)	(Fe)	(Cr)	
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.

Mn²⁺).⁴ Our results on the structure of FeVMoO₇ 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 structure¹¹ is due to inaccurate Mo—O bond lengths.

IR and Raman Spectra. The IR spectrum of FeVMoO₇ is consistent with that previously reported²⁰ and is similar to that of CrVMoO₇. The Raman spectra of FeVMoO₇ and CrVMoO₇ are presented in Figure 4. The Raman shifts and IR absorptions are listed in Table 5. Assignments 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 FeVMoO₇ and 982 cm⁻¹ for CrVMoO₇) 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 FeVMoO₇ and CrVMoO₇ respectively, and are consistent with the observed values according to the empirical equation²⁴

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

where ν is the Mo—O stretching frequency, and R is the Mo—O bond distance. The Raman shifts of 710 cm⁻¹ in FeVMoO₇ and 719 cm⁻¹ in CrVMoO₇ 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 [VMoO₇]³⁻ anions in the two compounds is reflected in the similarity of the Raman spectra in this region. However, three of these peaks in FeVMoO₇ 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 Fe³⁺. 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 FeVMoO₇ and 60–300 K for CrVMoO₇ revealed a Curie–Weiss behavior. The calculated $\mu_{\text{eff}} = 6.02 \mu_{\text{B}}$ (spin-only 5.92 μ_{B}) for FeVMoO₇ indicates that the Fe³⁺ ions (3d⁵) are in high-spin state. The calculated $\mu_{\text{eff}} = 3.95 \mu_{\text{B}}$ (spin-only 3.87 μ_{B}) for CrVMoO₇ indicates Cr³⁺ ions (3d³). The negative Weiss constants ($\theta = -51$ K for FeVMoO₇ and $\theta = -63$ K for CrVMoO₇) reveal antiferromagnetic interactions between the M³⁺ ions at 16 K and 34 K for FeVMoO₇ and CrVMoO₇, respectively.

Discussion

The structures of MVMoO₇ (M = Fe³⁺, Cr³⁺) display some rare and interesting characteristics. The most unusual characteristic is the complete ordering of V⁵⁺ and Mo⁶⁺ 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 situation is observed. Usually V⁵⁺ and Mo⁶⁺ are either completely disordered⁴ or at least partially disordered.²⁵

One consequence of the V⁵⁺/Mo⁶⁺ ordering, and perhaps the most interesting feature of the structure, is the presence of one-

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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. FeVMoO₇, CrVMoO₇, and MgMo₂O₇ are the only three known complex oxides containing such Mo–oxo double bonds. The simple oxide α -MoO₃ 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 MoO₃,²⁹ 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 -Bi₂Mo₃O₁₂. 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 MV-MoO₇ (M = Fe³⁺, Cr³⁺), the crystallographically observable Mo–oxo double bonds can serve as models for surface Raman

studies. Using the observed Mo=O bond distances in FeVMoO₇ and CrVMoO₇ 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 FeVMoO₇ and CrVMoO₇ 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.

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Supporting Information Available: Plots of the molar magnetic susceptibility and inverse susceptibility versus temperature for FeVMoO₇ and CrVMoO₇ (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.

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