Site-Specific Vanadates \( \text{Co}_4\text{Fe}_{3.33}(\text{VO}_4)_6 \) and \( \text{Mn}_3\text{Fe}_4(\text{VO}_4)_6 \)

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Single crystals of \( \text{Co}_4\text{Fe}_{3.33}(\text{VO}_4)_6 \) and \( \text{Mn}_3\text{Fe}_4(\text{VO}_4)_6 \) were grown from equivalent \( \text{CoO}/\text{Fe}_2\text{O}_3/\text{V}_2\text{O}_5 \) and \( \text{MnO}/\text{V}_2\text{O}_5 \) melts, respectively. The former crystallizes in the orthorhombic space group \( \text{Pnma} \) with parameters \( a = 4.965(1) \, \text{Å}, b = 10.211(1) \, \text{Å}, c = 17.188(3) \, \text{Å}, \) and \( Z = 2 \) and is a homeotype of such catalysts as \( \text{Mg}_2.5\text{VMoO}_8 \). The latter crystallizes in the triclinic space group \( \text{P} \) with parameters \( a = 6.703(2) \, \text{Å}, b = 8.137(1) \, \text{Å}, c = 9.801(2) \, \text{Å}, \alpha = 105.56(1)^\circ, \beta = 105.58(2)^\circ, \gamma = 102.35(1)^\circ, \) and \( Z = 1 \) and is a homeotype of \( \beta-\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6 \), the low-pressure form of \( \alpha-\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6 \). The cobalt analogue deviates in stoichiometry from the reactant melt to form the more dense \( \alpha-\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6 \) structure type comprised of partially occupied face-sharing octahedral and trigonal prismatic coordination sites.

Introduction

Multicomponent vanadates and molybdates can selectively oxidize hydrocarbons. For example, \( \text{(VO)}_2\text{P}_2\text{O}_7 \) and \( \text{SbVO}_4 \) are excellent catalysts for the oxidation of \( n \)-butane to maleic anhydride and ammoniation of propene to acrylonitrile, respectively. Our present aim is to gain a better understanding of the chemistry of this type of heterogeneous catalysis by developing new vanadates/molybdates. Single-crystal growth provides an effective way to discover and characterize new compounds because it renders thermodynamically favorable compositions and facilitates precise structural determination. Since the stoichiometry of the crystal is not restricted to that of the reactants, it can vary to facilitate the formation of particular structures, and the contributions to the stability of such structures can be elucidated by comparing the flux composition to that of the resulting crystals. Finally, characterization by X-ray analysis goes beyond basic structure to explicate critical details such as composition, defect chemistry, and atomic disorder.

Previous studies on the \( \text{MO}_x\text{V}_2\text{O}_7\text{MoO}_3 \) (\( \text{M} = \text{Mg, Zn, Co, Mn} \)) systems revealed that \( \text{Mg}_2.5\text{VMoO}_8 \) is a good catalyst for the oxidative dehydrogenation of butane to butene and butadiene,\(^9\) we have attempted to synthesize similar vanadates by substituting into \( \text{Cu}_3\text{Fe}_4(\text{VO}_4)_6 \). Attempts to replace CuO led us to investigate the \( \text{MO}_x\text{Fe}_2\text{O}_3 \) \( \text{V}_2\text{O}_5 \) (\( \text{M} = \text{Mg, Zn, Co, Mn} \)) systems since these divalent metals occur in the aforementioned vanadomolybdates. In the first two systems, the ternary vanadates \( \text{FeMg}_2\text{V}_3\text{O}_{11} \) and \( \text{FeZn}_2\text{V}_3\text{O}_{11} \) were found with the \( \text{GaZn}_2\text{V}_3\text{O}_{11} \) structure type.\(^11\) In the last two systems, the new ternary vanadates \( \text{Co}_4\text{Fe}_{3.33}(\text{VO}_4)_6 \) and \( \text{Mn}_3\text{Fe}_4(\text{VO}_4)_6 \) were found to be homeotypes of the \( \alpha-\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6 \) and \( \beta-\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6 \) structures, respectively. While these structures are reported here, the main goal of this paper is to communicate our understanding of the site-specific crystal chemistry which governs the formation of various structures and stoichiometries.

Experimental Section

Synthesis. Prior to crystal growth, a mixture of 1.345 g of \( \text{Co}_3\text{O}_4 \) \( \text{(certified reagent, Fisher)}, 1.756 \, \text{g of Fe}_2\text{O}_3 \) \( (99.4 \%, \text{Aldrich}) \), and 3.000 g of \( \text{V}_2\text{O}_5 \) \( (99.6 \%, \text{Aldrich}) \) powders were ground in an agate mortar and calcined in an alumina boat at 700 °C for 15 h in air. The oxygen content of cobalt oxide was determined by thermogravimetric analysis (TGA, TA Instruments Thermal Analyst 2000) in 7% \( \text{H}_2/93% \) \( \text{N}_2 \) at 800 °C for 3 h. The starting composition corresponds to \( \text{Co}_3\text{Fe}_4(\text{VO}_4)_6 \). The calcined powder was packed in a platinum crucible, heated at 180 °C h\(^{-1} \) to 1010 °C, cooled to 830 °C at 6 °C h\(^{-1} \), and further cooled to room temperature at 120 °C h\(^{-1} \). Many dark needle crystals were formed on the top of melt. A total weight loss of 13.5% was observed owing to the evaporation of vanadium oxide and loss of oxygen from cobalt oxide. Powder X-ray diffraction (XRD) data of the crystals revealed a pattern similar to that of \( \text{Mg}_2.5\text{VMoO}_8 \). The melting point of the powdered crystals was determined by differential thermal analysis (DTA) to be 995 °C in static air. This compound melts incongruently and becomes completely liquid above 1017 °C. The

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average atomic ratios of the metal species in the crystals were
determined by energy dispersive analysis of X-ray (EDAX, Hitachi,
Pioneer S-4500 SEM) to be Co:V = 4.1:3.4:6.0 indicative of the
stoichiometry Co$_4$Fe$_3$(VO$_4$)$_6$. The atomic ratio Co:V of the
investigated crystal was also determined by ICP-AES (inductively
coupled plasma atomic emission spectrophotometry, Thermo Jarrell Ash,

About 10 g of polycrystalline Co$_4$Fe$_3$(VO$_4$)$_6$ was prepared via
standard solid-state reaction of CoO$_2$, Fe$_2$O$_3$, and V$_2$O$_5$. Stoichiometric
amounts of the oxides were ground in an agate mortar and
calced at 670 °C for 30 h. The samples were reground, pressed into
pellets, and heated in an alumina boat at 900 °C for 11 h and then 930
°C for 55 h. Each pellet increased about 70% in volume presumably
due to the evolution of oxygen from cobalt oxide during the heating
procedure.

Mn$_3$Fe$_4$(VO$_4$)$_6$ crystals were grown by melting a mixture of 1.758 g
of Mn$_2$O$_3$ (99.9%, ERAC), 2.370 g of Fe$_2$O$_3$, and 4.050 g of V$_2$O$_5$
which corresponds to the composition “Mn$_3$Fe$_4$(VO$_4$)$_6$”. A platinum
 crucible was used to preheat the mixture at 670 °C for 18 h in air to
allow the three oxides to react with each other and reduce the
evacuation of vanadium oxide. The mixture was then heated at 1050
°C for 2 h, cooled to 800 °C at 6 °C h$^{-1}$, and finally cooled to room
temperature at 120 °C h$^{-1}$ all in flowing argon. This atmosphere
promotes the formation of Mn$_3$Fe$_4$(VO$_4$)$_6$ by reducing Mn$^{3+}$ to Mn$^{2+}$.
A total weight loss of 2.4% was observed owing to the evaporation of
vanadium oxide and loss of oxygen from Mn$_2$O$_3$. Dark crystals were
readily separated from the rest of melt, and the atomic ratios were
determined by EDAX to be Mn:Fe:V = 3.1:4:3.6:0, indicative of
Mn$_3$Fe$_4$(VO$_4$)$_6$.

Polycrystalline Mn$_3$Fe$_4$(VO$_4$)$_6$ was prepared via solid-state reaction
of Mn$_2$O$_3$, Fe$_2$O$_3$, and V$_2$O$_5$ at 870 °C for 48 h in flowing nitrogen.
The weight loss during the formation of Mn$_3$Fe$_4$(VO$_4$)$_6$ was monitored
by TGA at 800 °C for 5 h under nitrogen. The total weight loss of
2.3% is consistent with the calculated value 2.2% for the reduction of
Mn$^{3+}$ to Mn$^{2+}$. The melting point of Mn$_3$Fe$_4$(VO$_4$)$_6$ was determined
by DTA to be 918 °C in air.

Crystallographic Determination. A dark Co$_4$Fe$_3$(VO$_4$)$_6$ needle
(0.70 × 0.08 × 0.20 mm$^3$) and a dark Mn$_3$Fe$_4$(VO$_4$)$_6$ prism (0.38 ×
0.35 × 0.20 mm$^3$) were mounted on glass fibers for study by single-
crystal X-ray diffraction. All measurements were made on an Enraf-
Nonius CAD4 diffractometer with graphite-monochromated Mo K$_\alpha$
radiation. Details of the structure determinations and refinements are
listed in Table 1. Analytical absorption corrections were applied, which
resulted in transmission factor ranges of 0.48–0.83 for Co$_4$Fe$_3$(VO$_4$)$_6$
and 0.09–0.26 for Mn$_3$Fe$_4$(VO$_4$)$_6$.

The observed systematic absences (0kl, k + l = 2n + 1; hkl, h
= 2n + 1) for Co$_4$Fe$_3$(VO$_4$)$_6$ are consistent with the space groups Pnma

Table 1. Crystallographic Data

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<tr>
<th>atom</th>
<th>pos</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B$<em>0$/B$</em>{iso}$ (Å$^2$)</th>
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<td>$0.20491(4)$</td>
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* See Table 2.

and Mn$_2$O$_3$. The structure was solved by direct methods and
expanded using Fourier techniques. It refined satisfactorily in the centro-
symmetric space group Pnma. All atoms were refined anisotropically except
for the disordered atoms Co(1) and Fe(1). The formula was confirmed by
crystal chemical analysis and population refinements. Similarly, the structure
of Mn$_3$Fe$_4$(VO$_4$)$_6$ was solved in the space group $P1$. All atoms were
refined anisotropically. Population refinements indicate that disordering
between Fe$^{3+}$ and Mn$^{2+}$ does not take place. All calculations were
performed using the TEXSAN crystallographic software package of
Molecular Structure Corp. Atomic positions, thermal displacement
parameters, and occupancies are presented in Tables 2 and 3.

X-ray Measurements. XRD data for polycrystalline Co$_4$Fe$_3$(VO$_4$)$_6$
and Mn$_3$Fe$_4$(VO$_4$)$_6$ were collected on a Rigaku X-ray diffractometer
with Cu K$_\alpha$ radiation and nickel filter in the 2θ range of 10–60° (step
scan: 0.05°/4 s, Si as internal standard) at 25 °C. The observed and calculated
$\bar{d}_{	ext{calc}}$ values and relative intensities $I_{	ext{rel}}$ for the powder XRD
patterns of Co$_4$Fe$_3$(VO$_4$)$_6$ and Mn$_3$Fe$_4$(VO$_4$)$_6$ are given in the Supporting
Information. The calculated unit cell parameters agree with the values from the single-crystal refinements.

Sheldrick, G. M. SHELXL86. In Crystallographic Computing 3;
Sheldrick, G. M., Kräger, C., Goddard, R., Eds.; Oxford University

Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-
In The DIRDIF program system; Technical Report of the Crystal-
lography Laboratory; University of Nijmegen: Nijmegen, The Neth-

(15) TEXSAN: Crystal Structure Analysis Package; Molecular Structure

Results and Discussion

Structure of Co$_4$Fe$_{3.33}$(VO$_4$)$_6$ viewed along the a axis

Co$_4$Fe$_{3.33}$(VO$_4$)$_6$. The basic strategy for crystal growth mimics that for Mg$_{2.5}$VMoO$_8$. Both the flux composition, “Co$_2$Fe$_2$-(VO$_4$)$_6$”, and the crystal composition, Co$_4$Fe$_{3.33}$(VO$_4$)$_6$, are located on the line between Co$_2$V$_2$O$_8$ and FeVO$_4$ in the CoO−Fe$_2$O$_3$−V$_2$O$_3$ system. Any composition along this line can be written as Co$_{1+x}$Fe$_{6-x}$(VO$_4$)$_6$. “(Co$_2$Fe$_2$)(VO$_4$)$_6$” and Co$_4$Fe$_{3.33}$(VO$_4$)$_6$ correspond to $x = 1$ and $x = 1.33$, respectively. Notice that the amount of vanadium does not change relative to the oxygen content but that the amount of low-valent cations increases. This is the opposite of the Mg$_{2.5}$VMoO$_8$ case in which the crystals (Mg$_{6+y}$Mo$_{6-y}$V$_2$O$_{24}$, $y = 1.5$) contain less low-valent cations per O$_2$ than the starting composition (Mg$_{6+y}$Mo$_{6-y}$V$_2$O$_{24}$, $y = 2$). In both cases the final structure is the same and the ratio of low-valent cations to high-valent cations approaches 1.23 while the oxygen content remains constant.

Co$_4$Fe$_{3.33}$(VO$_4$)$_6$ is a homotype of NaCo$_{2.31}$(MoO$_4$)$_2$, Mg$_{2.5}$VMoO$_8$, and lyonsite, α-Cu$_3$Fe$_4$(VO$_4$)$_6$. The oxygen framework for this structure creates three different cation sites for low-valent cations (oxidation state I, II, or III): face-shared octahedral sites, edge/corner-shared octahedral sites, and edge-shared trigonal prismatic sites (Figure 1 and Table 4). In addition, high-valent cations (V$^{5+}$, Mo$^{6+}$, V$^{5+}$/Mo$^{6+}$, or V$^{5+}$/W$^{6+}$) occupy two types of isolated tetrahedral sites within the framework. The details of the oxygen connectivity with the high-valent cations have been described previously for Mg$_{2.5}$VMoO$_8$.

The title compound can be written out in terms of the framework sites described above: [Co(2)$_2$V$_2$O$_8$][Co(1)$_8$Fe(1)$_8$O$_{32}$][Co(3)$_4$]V$_6$. The face-shared octahedral site is $2/2$ occupied by Co which is the lowest occupation observed except for in α-Cu$_3$Fe$_4$(VO$_4$)$_6$.

A defining characteristic of this structure type is the high ratio of low-valent cations to high-valent cations. All synthesized examples to date exhibit a ratio between 1.22 and 1.27 which corresponds to an occupancy on the face-shared site between 0.66 and 0.81, respectively, when the other sites are fully occupied. The structure of Co$_4$Fe$_{3.33}$(VO$_4$)$_6$ achieves a 1.22 ratio of Co/Fe to V by incorporating extra Co$^{2+}$ and less Fe$^{3+}$ relative to the reactant stoichiometry (ratio = 1.17). This is the only known example of this type of behavior in these iron/vanadium...

Table 4. Selected Distances and Bond Angles for Co$_4$Fe$_{3.33}$(VO$_4$)$_6$

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Figure 3. Connections of MnO₄ and MnO₅ polyhedra with Fe₂O₁₀ octahedral dimers in Mn₃Fe₄(VO₄)₆.

Table 5. Selected Distances and Bond Angles for Mn₃Fe₄(VO₄)₆

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<th>Bond angles (deg)</th>
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<td>Mn₂–O(2) 2.113(4)</td>
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The Fe₂O₁₀ octahedral dimers are surrounded by either 8 Fe₂O₁₀ edge-shared octahedra. The double corner connection of Fe₁O₁₀ to V₂O₄ (Figure 4a) is rare because usually the distance between two vertexes of a VO₄ tetrahedron is not long enough to span the two apices of an Fe₂O₁₀ edge-shared octahedron. The Fe₁–Fe₁ distance (3.121 Å) is significantly shorter than the Fe₁–Fe₂ (3.212 Å), as well as the corresponding distances in isolated Fe₂O₁₀ dimers found in Fe₅MoO₁₇, Fe₅V₂MoO₁₇, and Fe₂V₂O₄. Within each MnO₆ unit two bonds are substantially elongated, indicating a strong octahedral distortion. Such a distortion could be a Jahn–Teller effect if the Mn is +3. Structural refinement, bond valence calculations (see Table 3), and TGA weight loss all concur however that not only is the iron Fe⁴⁺ and the vanadium V⁵⁺ but that the manganese is Mn⁵⁺. Therefore, the distortion must be attributed to interpolyhedral connections, as observed in Mn₃O₃(SeO₄)₂. It is likely that the position of the crystallographically independent oxygen (O(7)) is determined by other polyhedra. This explanation is supported by the presence of the CuO₄ square planes in β-Cu₃Fe₄(VO₄)₆. O(7) also has relatively large temperature factor (Table 3), and the thermal ellipsoid elongates in the direction of the manganese bonds. Since Mn⁵⁺ is a d⁵ cation, the enlarged temperature factor in the octahedra is likely due to these same interpolyhedral stresses and negligible ligand field stabilization.

MnO₄ square pyramids are quite common, being found in brownmillerite-related compounds such as Ca₂Mn₂O₅, and Ca₂MnO₅. But MnO₄ trigonal bipyramids are very unusual. To our knowledge, the only MnO₅ trigonal bipyramids reported exist in such oxides as Lu₃MnFeO₁₀ and Lu₃MnFeO₁₀, where the manganese is disordered with the iron. The bond angles in the title compound do deviate slightly from ideal trigonal bipyramidal coordination toward square pyramidal geometry.

The ratio of low-valent cations to high-valent cations in the manganese phase is 1.17 and does not differ from the reactant stoichiometry. This indicates either the unavailability of the α-CuFe₄(VO₄)₆ structure type or the particular stability of the β-Cu₃Fe₄(VO₄)₆ structure type for the manganese case. The former possibility is debased by the fact that Mn⁵⁺ is known to occupy the face-shared octahedral and trigonal prismatic sites of the β-CuFe₄(VO₄)₆ structure type in Mn₂₋CuFe₄(VO₄)₆.

**General Comments.** The molar density of Co₅Fe₃(VO₄)₆ is greater than that of Mn₃Fe₄(VO₄)₆. This is a result of the

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higher coordination of the anions and cations. α-Cu₃Fe₄(VO₄)₆ (d = 4.21 g/cm³) is also more closely packed than β-Cu₃Fe₄-(VO₄)₆ (d = 3.97 g/cm³) and is regarded as the high-pressure form. As previously noted, it is likely that the α-Cu₃Fe₄(VO₄)₆ structure type is available to the manganese analogue and so should be stable under pressure. It is also possible that stabilization could be achieved by simply choosing a flux stoichiometry with more low-valent cations. As reported in this paper, the more dense cobalt analogue forms directly at ambient pressure from an off-stoichiometric starting mix. Making the less dense cobalt analogue is likely impossible unless it can be synthesized by choosing a reactant flux with even less low-valent cation, i.e. even farther from the necessary composition for the more dense phase.

The four MO–Fe₂O₃–V₂O₅ (M = Mg, Zn, Co, Mn) systems yielded four new ternary vanadates with three different structures, but it is worthwhile to note which compounds did not form. Since growing crystals from mixed oxide fluxes generally renders thermodynamic products, it can be concluded that many of the possible polymorphic compounds within these systems are relatively unstable despite the fact that they are quite similar. The cobalt system is the only example of a structure that incorporated additional low-valent cations into an optimally dense structure. The manganese system maintained the reactant stoichiometry, while the zinc and magnesium systems expunged low-valent cations to form crystals with ratios of low-valent to high-valent cations equal to one. It can be inferred, consequently, that the two Cu₃Fe₄(VO₄)₆ structure types are destabilized by zinc and magnesium. The stabilities of site-specific cation occupation are the link between structure and composition. The more dense structures create less common coordination environments such as face-shared octahedra, trigonal prisms, and trigonal bipyramids and, therefore, require cations to occupy these sites at least partially. The formation of the high-density structure in general must be a complex function of composition. The fact that compounds with compositions such as “Mg₃Fe₄(VO₄)₆”, “Zn₃Fe₂V₃(VO₄)₆”, “FeCo₂V₁O₁₁”, and “FeMn₂V₁O₁₁” were not detected illustrates the intricacies and suggests the possibilities of the solid-state chemistry involved.

Conclusions

Crystals of Co₃Fe₁.₃₃(VO₄)₆ and Mn₃Fe₄(VO₄)₆ were successfully grown from mixed metal oxide melts. Single-crystal X-ray diffraction studies revealed the details of the two structures, which have been discussed and compared with two polymorphs of Cu₃Fe₄(VO₄)₆ as well as other similar structures. In addition, the rare Mn⁵⁺O₅ trigonal bipyramidal coordination was also discussed. Detailed phase diagrams of Co/MnO–Fe₂O₃–V₂O₅ and catalytic properties for the title compounds are under investigation.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, as well as tables of observed and calculated X-ray powder diffraction data. This material is available free of charge via the Internet at http://pubs.acs.org.