NaV₃(OH)₆(SO₄)₂: A Kagomé-Type Vanadium(III) Compound with Strong Intralayer Ferromagnetic Interactions**

Daniel Grohol, Dimitris Papoutsakis, and
Daniel G. Nocera*

Extended vanadium compounds typically exhibit an antiferromagnetic spin ordering among d^1 or mixed-valence d^0/d^1 centers. In these systems, spins interact through superexchange pathways comprising neighboring vanadium subunits linked by atoms or groups. The majority of these materials are composed of layered networks of interconnected square pyramids, which result from the termination of the z axis of the vanadium coordination sphere by a strong axial ligand (usually oxo of vanadyl).[1–5] The occurrence of ferromagnetic coupling in layered vanadium compounds is rare. Only vestiges of ferromagnetism have been observed in layers composed of square-pyramidal d^1 or mixed-valence d^0/d^1 vanadium centers.[5–8] For the d^2 electron count, ferromagnetic interactions have been observed, but they usually arise from the secondary effect of canted, antiferromagnetically aligned spins.[9–11] Primary ferromagnetic interactions are implicated in short-range pairwise interactions between V^{III} centers of various binuclear compounds.[12–15] However, we are not aware of primary ferromagnetic interactions between V^{III} centers in an extended layered material. Owing to our interest in developing the magnetism of layered vanadium compounds, we turned our attention to utilizing the lattice of the jarosite mineral ($AFe_3(OH)_6(SO_4)_2$, A is usually an monovalent cation)[16] to stabilize d^2 vanadium centers in a layered environment. We now report a new hydrothermal synthesis that has enabled us to prepare and to structurally characterize a stoichiometrically pure jarosite-type compound of vanadium(III), $NaV_3(OH)_6(SO_4)_2$. Preliminary magnetic measurements reveal the unprecedented circumstance of strong ferromagnetic coupling between vanadium ions in a layered architecture.

Jarosite-type materials are notoriously difficult to prepare in pure form. Synthetic methods have relied on the precipitation of jarosite from hydrolyzed acidic solutions of sulfate anions and monovalent and trivalent cations.[17] The monovalent cations are often replaced by hydronium ions and the coverage of the trivalent sites is incomplete (83–95% occupation).[18, 19] Owing to these site defects, the magnetic behavior of jarosites has historically been sample dependent.[18] With the goal of acquiring reproducible and self-consistent magnetic measurements, we sought to develop new synthetic methods that would reliably afford complete lattice coverage in jarosite-type compounds. Our approach focuses on assembling the jarosite framework by hydrothermal oxidation–reduction methods.

The vanadium congener of jarosite, $NaV_3(OH)_6(SO_4)_2$, has been prepared according to Equation (1).

$$4\,VCl_4 + 8\,H_2O + 2\,Na_2SO_3 \longrightarrow$$
$$NaV_3(OH)_6(SO_4)_2 + V^{3+} + 3\,Na^+ + 16\,Cl^- + 10\,H^+ \quad (1)$$
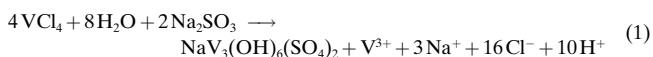
Reduction of V^{IV} with sulfite under acidic conditions (pH ∼ 1.5) affords the title compound, which is obtained stoichiometrically pure and in single crystalline form. This redox method allows us to minimize site defects by selective reduction of the vanadium starting compound to the $+3$ oxidation state. Also, in contradistinction to nonredox precipitation methods, the introduction of a redox step prior to precipitation allows the crystallization of the material to be more easily controlled.

$NaV_3(OH)_6(SO_4)_2$ crystallizes in the rhombohedral space group $R\bar{3}m$.[20] A crystallographically unique V^{III} ion resides in a distorted octahedron, composed of four equatorial oxygen atoms (O3) from the bridging hydroxy groups and of two axial oxygen atoms (O2) from the capping sulfate groups (Figure 1, top). The vanadium pseudooctahedron is tetragonally elongated along its z axis. The bridging hydroxy groups connect V^{III} ions with a V-O3-V angle of 132.6(2)° to form a triangular μ-hydroxy trimer capped by the sulfate anion, which assumes an almost ideal tetrahedral geometry. A residual electron
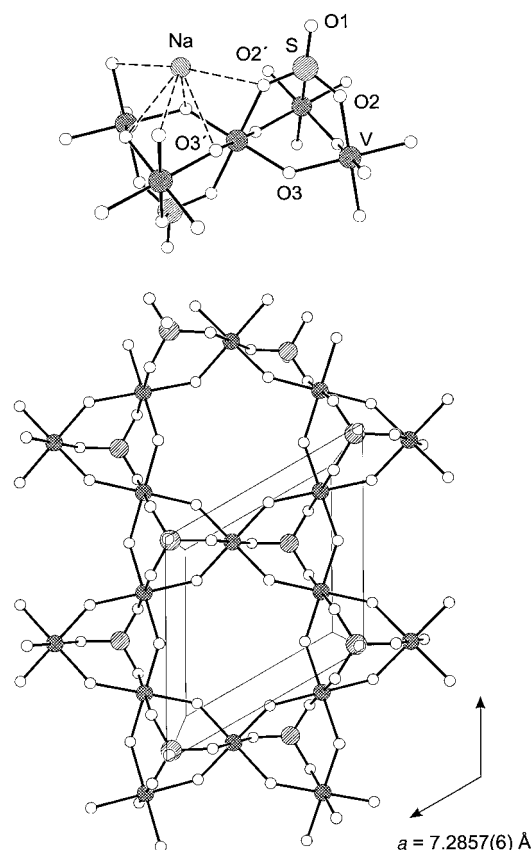

Figure 1. The X-ray crystal structure of a layer segment of $NaV_3(OH)_6$-$(SO_4)_2$. The magnetic subunit of a triangular μ-hydroxyvanadium trimer, capped by a sulfate anion, is shown at the top of the figure. Selected bond lengths [Å] and angles [°]: V-O2 2.054(4), V-O3 1.989(2), S-O1 1.461(8), S-O2 1.476(5); O2-V-O3 92.5(1), O3-V-O3′ 90.9(3).

[*] Prof. D. G. Nocera, D. Grohol, D. Papoutsakis
Department of Chemistry, 6-335
Massachusetts Institute of Technology
Cambridge, MA 02139 (USA)
Fax: (+1) 617-253-7670
E-mail: nocera@mit.edu

peak of 0.63 e Å^{-3} at a distance of 0.89 Å from O3 indicates the presence of a hydrogen atom from the μ-hydroxy group; neutron diffraction studies confirm its location.[21] The vanadium trimers are linked at their corners to form a Kagomé lattice[19] in a two-dimensional hexagonal network (Figure 1, bottom). The sulfate capping groups alternately point up and down about the hexagonal network. The Kagomé layers are separated by a crystallographically unique sodium atom (d spacing 5.617(1) Å), which resides in the interlayer space with the same x,y coordinates as the sulfur atom. Six sulfate oxygen atoms ($d_{Na-O2} = 2.949(5)$ Å) and six hydroxy oxygen atoms ($d_{Na-O3} = 2.756(4)$ Å) surround each sodium ion.

Figure 2 shows temperature-dependent magnetic susceptibilities for NaV$_3$(OH)$_6$(SO$_4$)$_2$ at varying applied field strengths. At 0.5 kOe, M/H increases upon cooling to a sharp
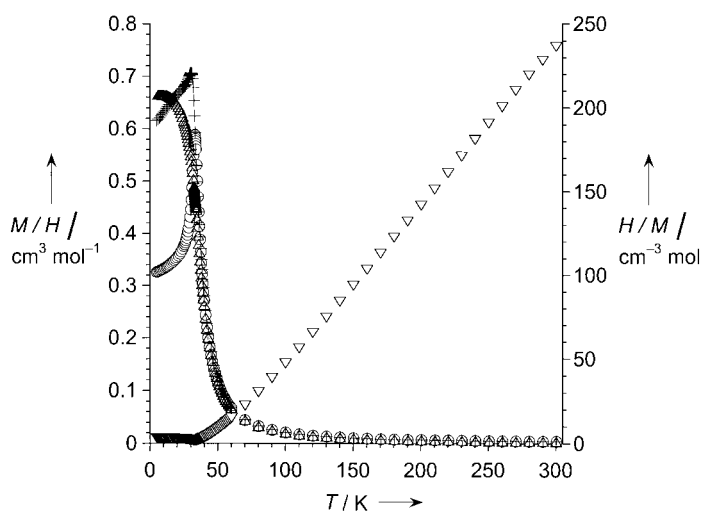

Figure 2. Temperature dependence of M/H per mole of vanadium atoms for NaV$_3$(OH)$_6$(SO$_4$)$_2$ at applied magnetic field strengths of 0.5 ($\circ$), 5.0 (+), and 10.0 ($\triangle$) kOe. The H/M versus T plot ($\triangledown$) was measured at an applied field of 0.5 kOe.

maximum at $T_N = 33.3$ K, followed by a downturn. At a field strength of 10 kOe, M/H increases monotonically with decreasing temperature. The M/H curve exhibits intermediate behavior when measurements are performed in an external field of 5 kOe; a blunt maximum is observed in the curve at 30.3 K. Plots of H/M versus T (150–300 K) yield a Weiss constant of $+53(2)$ K for the three applied fields. This large and positive value indicates appreciable intralayer ferromagnetic interactions between neighboring V^{III} centers.

The field-dependence observed in Figure 2 is ascribed to strong intralayer ferromagnetic interactions and weak, field-dependent interlayer interactions. This behavior is characteristic of metamagnetism,[22–24] which more commonly prevails for layered halides and hydroxides of divalent ions.[25] We propose that a dominant ferromagnetic exchange interaction propagates about the magnetic sites of the triangular Kagomé lattice through the bridging hydroxy groups. In weak fields, the layers couple antiferromagnetically at $T < T_N$. As the applied field is increased, this weak antiferromagnetic coupling of spins between neighboring layers is overwhelmed, leading to the eradication of T_N.

The occurrence of ferromagnetic Kagomé layers is unusual and at variance with the antiferromagnetic exchange observed for jarosite and its derivatives.[18, 26–29] Inasmuch as the V^{III} jarosite is isostructural with the Cr^{III} and Fe^{III} analogues, the ferromagnetism of NaV$_3$(OH)$_6$(SO$_4$)$_2$ likely arises from the d^2 electron count of the V^{III} centers. Two electrons in an axially elongated octahedron will reside in d$_{xz}$ and d$_{yz}$ orbitals. Orbital symmetry models for superexchange[30, 31] suggest the intralayer ferromagnetism to arise from coupling along a pathway involving metal d-π and hydroxy p orbitals. Current studies are aimed at acquiring a more detailed understanding of the magnetic properties of NaV$_3$(OH)$_6$(SO$_4$)$_2$ and its related alkali metal derivatives.

Experimental Section

A 2.0 M solution of VOCl$_2$ in 4.0 M HCl was prepared by the dropwise addition of VCl$_4$ (5.3 mL; Aldrich) to a small amount of ice-cold water while stirring, and diluting to 25 mL. A 2.0 mL aliquot of this solution (4 mmol of VOCl$_2$) was transferred into the Teflon container of a 23 mL Parr pressure bomb. In a separate beaker, Na$_2$SO$_3$ (0.227 g, 1.8 mmol), NaOH (0.20 g, 5.0 mmol), and NaCl (0.117 g, 2.0 mmol) were dissolved in distilled water (8 mL). This mixture was slowly added to the Teflon container containing the VOCl$_2$ solution. The bomb was enclosed and placed into an oven at 202 °C and the mixture was allowed to react for three days. The oven was subsequently cooled to room temperature at a 0.1 °C min^{-1} rate. Small, dark red crystals were filtered washed, and dried in air (yield 22 %). Elemental analysis for NaV$_3$(OH)$_6$(SO$_4$)$_2$: calcd: H 1.28, Na 4.89, V 32.51, S 13.64; found: H 1.32, Na 5.06, V 32.85, S 13.88.

Magnetic susceptibility measurements were performed on powder specimens on a SQUID magnetometer (Quantum Design MPMSR2). The temperature dependence of the magnetization M was acquired in external fields of 0.5, 5.0, and 10.0 kOe. At low field strength, M varies linearly with the field H, and M/H represents the magnetic susceptibility of the material. As expected for materials exhibiting strong ferromagnetic interactions,[32] M/H does not represent the actual susceptibility at high fields owing to the nonlinearity of magnetization with field strength.

[1] A. Clearfield, *Prog. Inorg. Chem.* **1998**, *47*, 371.
[2] J. Le Bideau, D. Papoutsakis, J. E. Jackson, D. G. Nocera, *J. Am. Chem. Soc.* **1997**, *119*, 1313.
[3] P. Amoros, M. D. Marcos, A. Beltrán-Porter, D. Beltrán-Porter, *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 123.
[4] D. Beltrán, A. Beltrán, P. Amorós, R. Ibáñez, E. Martínez, A. Le Bail, G. Ferey, G. Villeneuve, *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 131.
[5] D. Beltrán-Porter, P. Amorós, R. Ibáñez, A. Le Bail, G. Ferey, G. Villeneuve, *Solid State Ionics* **1989**, *32*, 57.
[6] G. Villeneuve, L. Lezama, *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 495.
[7] D. Papoutsakis, J. E. Jackson, D. G. Nocera, *Inorg. Chem.* **1996**, *35*, 800.
[8] T. Yamase T, H. Makino *J. Chem. Soc. Dalton Trans.* **2000**, *7*, 1143.
[9] H. C. Nguyen, J. B. Goodenough, *Phys. Rev. B* **1995**, *52*, 324.
[10] Y. Ren, T. T. M. Palstra, D. I. Khomskii, E. Pellegrin, A. A. Nugroho, A. A. Menovsky, G. A. Sawatzky, *Nature* **1998**, *396*, 441.
[11] Y. Kanke, *Phys. Rev. B* **1999**, *60*, 3764.
[12] H. Weihe, H. U. Güdel, *J. Am. Chem. Soc.* **1998**, *120*, 2870.
[13] P. Knopp, K. Wieghardt, *Inorg. Chem.* **1991**, *30*, 4061.
[14] P. Knopp, K. Wieghardt, B. Nuber, J. Weiss, W. Sheldrick, *Inorg. Chem.* **1990**, *29*, 363.
[15] C. J. Carrano, R. Verastgue, M. R. Bond, *Inorg. Chem.* **1993**, *32*, 3589.
[16] Jarosite is a member of the alunite supergroup of minerals, AG$_3$-(OH,OH$_2$)$_6$(TO$_4$)$_2$, where A is a mono-, di-, or trivalent cation with a coordination number ≥ 9, G is an octahedrally coordinated metal trication, and T is S^{6+}, Cr^{6+}, P^{5+}, or As^{5+} in an oxygen tetrahedron. For details see: J. L. Jambor, *Can. Mineral.* **1999**, *37*, 1323
[17] J. E. Dutrizac, *Met. Trans. B* **1983**, *14*, 531.

[18] A. S. Wills, A. Harrison, C. Ritter, R. I. Smith, *Phys. Rev. B* **2000**, *61*, 6156.

[19] A. S. Wills, A. Harrison, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2161.

[20] Crystallographic data for $NaV_3(OH)_6(SO_4)_2$: Rhombohedral, space group $R\bar{3}m$, $a = b = 7.2857(6)$, $c = 16.851(2)$ Å, $V = 774.6(1)$ Å^3, $Z = 3$, $\rho_{calcd} = 3.023$ g cm^{-3}, $F(000) = 672$, $\lambda(Mo_{K\alpha}) = 0.7107$ Å, crystal dimensions $0.04 \times 0.04 \times 0.01$ mm. A total of 1050 reflections were collected at $-90\,^{\circ}C$ using a Siemens diffractometer equipped with a CCD detector in the θ range of 3.45° to 23.25°, of which 161 were unique ($R_{int} = 0.0351$). The structure was solved by the Patterson heavy atom method in conjunction with standard difference Fourier techniques and all heavy atoms were refined anisotropically (25 parameters). Hydrogen atoms were not included in the refinement. The least squares refinement based on F^2 converged normally giving residuals of $R = 0.0306$, $wR2 = 0.0792$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411658.

[21] D. Grohol, B. H. Toby, Q. Z. Huang, J. W. Lynn, D. G. Nocera, unpublished results.

[22] M. Kurmoo, *Philos. Trans. R. Soc. London A* **1999**, *357*, 3041.

[23] R. L. Carlin, *Magnetochemistry*, Springer, Berlin, **1986**.

[24] E. Stryjewski, N. Giordano, *Adv. Phys.* **1977**, *26*, 487.

[25] K. Agawa, E. Coronado, M. Drillon, *MRS Bull.* **2000**, *25*, 52.

[26] T. Inami, M. Nishiyama, S. Maegawa, Y. Oka, *Phys. Rev. B* **2000**, *61*, 12181.

[27] S. A. Earle, A. P. Ramirez, R. J. Cava, *Physica B* **1999**, *262*, 199.

[28] S.-H. Lee, C. Broholm, M. F. Collins, L. Heller, A. P. Ramirez, C. Kloc, E. Bucher, R. W. Erwin, N. Lacevic, *Phys. Rev. B* **1997**, *56*, 8091.

[29] A. Keren, K. Kojima, L. P. Le, G. M. Luke, W. D. Wu, Y. J. Uemura, M. Takano, H. Dabkowska, M. J. P. Gingras, *Phys. Rev. B* **1996**, *53*, 6451.

[30] J. B. Goodenough, *Magnetism and the Chemical Bond*, Krieger, Huntington, NY, **1976**.

[31] O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**.

[32] G. C. DeFotis, E. M. McGhee, I. Bernal, D. B. Losee, *J. Appl. Phys.* **1987**, *61*, 3298.

Neutral Cyclooctasulfur as a Polydentate Ligand: Supramolecular Structures of [Rh₂(O₂CCF₃)₄]ₙ(S₈)ₘ (n:m = 1:1, 3:2)**

F. Albert Cotton,* Evgeny V. Dikarev, and Marina A. Petrukhina

It is not unreasonable to suppose that the S_8 molecule, with two lone pairs of electrons on each atom, would be able to function as a Lewis base—even as a multidentate Lewis base. And yet, no structurally characterized example of coordination of the cyclooctasulfur ligand to a transition metal

[*] Prof. F. A. Cotton, Dr. E. V. Dikarev, Dr. M. A. Petrukhina
Laboratory for Molecular Structure and Bonding
Department of Chemistry, Texas A&M University
P.O. Box 30012, College Station, TX 77842-3012 (USA)
Fax: (+1) 979-845-9351
E-mail: cotton@tamu.edu

complex is reported. There are several cases in which S_8 rings cocrystallize with other molecules, not covalently bound but merely packed into the crystal. These solid inclusion compounds with transition metal complexes are: $[Cu(C_{12}H_8N_2)_2I]I \cdot S_8$,[1a] $[WCl_4S] \cdot S_8$[1b] and $[WCl_4S(thf)] \cdot S_8$,[1c] $[Co_6(\mu\text{-}S)_8(CO)_6] \cdot 3 S_8$,[1d] $[Cu_4(S_5)_2(C_5H_5N)_4] \cdot S_8$,[1e] $[\{Pt_2X(5\text{-mpyt})_4\}_2(\mu\text{-}S_4)] \cdot 0.5 S_8$ (X = Cl, Br; 5-mpyt = 5-methylpyridine-2-thiolate),[1f] $[M(TMTAA)_2] \cdot S_8$ (M = Cu, Ni; TMTAA = 5,7,12,14-tetramethyldibenzo[*b*,*i*]-1,4,8,11-tetraaza[14]annulenate),[1g] $[Na\text{-}[15]crown\text{-}5]_2[(TaSCl_4)_2dioxane] \cdot S_8$.[1h]

What may well be a compound with a covalently bound S_8 molecule, $[Re_2X_2(CO)_6(S_8)]$ (X = Br, I), was reported by W. Baratta and F. Calderazzo,[2] but a crystal structure was not obtained. A few years later they were able to isolate the $[Re_2I_2(CO)_6(Se_7)]$ complex[3] and to show by X-ray crystallography that it contains an $\eta^2\text{-}\mu_2\text{-}Se_7$ ring. They suggested that $[Re_2X_2(CO)_6(S_8)]$ may have a similar dinuclear structure with bridging halides and an η^2-coordinated cyclooctasulfur unit. In addition, the S_8 molecule is known[4] to coordinate to the d^{10} silver(I) ion in $[Ag(S_8)_2](AsF_6)$. As far as we know there is no other literature dealing with compounds of transition metals that contain neutral S_8 molecules as ligands. However, elemental sulfur is clearly a candidate (along with H_2 and halogens) to add coordinatively to transition metal centers, possibly as a preliminary step to the completion of an oxidative-addition process. As we have already successfully isolated and characterized a remarkable adduct of molecular diiodine with a powerful bidentate Lewis acid, dirhodium(II) tetra(trifluoroacetate), in the form of the one-dimensional (1D) chain complex $[Rh_2(O_2CCF_3)_4 \cdot I_2]_\infty$,[5] we decided to extend that approach to elemental sulfur.

The preparation of products and growth of X-ray quality crystals have been achieved by using a solventless technique[6] based on a sublimation–deposition procedure, in which volatile dirhodium(II) tetra(trifluoroacetate) was employed in the presence of vapors of elemental sulfur. For the latter, the thermodynamically stable form in the vapor phase at the temperatures employed is known to be S_8 molecules.[7] Working with different ratios of Rh_2 to S_8 in the initial mixtures (from equimolar quantities to lower concentrations of S_8) we have successfully isolated two sulfur adducts of $[Rh_2(O_2CCF_3)_4]$. The stoichiometries of the two products $[Rh_2(O_2CCF_3)_4]_n(S_8)_m$ have been found by chemical analyses to be $n:m = 1:1$ for **1** and $n:m = 3:2$ for **2**. The new coordination compounds are relatively stable under moderate conditions, insoluble in organic solvents at room temperature, destroyed by coordinating solvents, and slowly decomposed even by noncoordinating dichloromethane to release elemental sulfur. Products **1** and **2** have been examined by X-ray crystallography.

The structure of **1** consists[8] of dirhodium(II) tetra(trifluoroacetate) units with the eight-membered S_8 cycles 1,3-attached to their axial positions to form a zigzag 1D chain (Figure 1). Each rhodium atom of the Rh_2 unit coordinates to one sulfur atom of an S_8 molecule; the two Rh–S distances at the ends of the dimetal unit are similar, 2.516(1) and 2.578(1) Å.

The structure of **2** is particularly interesting[9] as each S_8 molecule is 1,3,6-coordinated to three dirhodium complexes, while each Rh_2 unit binds to two different octasulfur rings.