Vanadium–Sulfite Polyoxometalates

Polyoxovanadium(IV) Sulfite Compounds: Synthesis, Structural, and Physical Studies**

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Dedicated to Professor Dieter Rehder on the occasion of his 60th birthday

The current interest in polyoxometalate chemistry is representative of the diverse nature of this family of inorganic clusters, which exhibit a wide variety of compositions and have considerable structural versatility,[1] as well as important magnetic,[2] optical,[1] and catalytic properties.[1] Much attention has been paid to heteropolyanions that contain tetrahedral phosphate groups.[3] While a number of research groups have focussed on polyoxomolybdenum and vanadium phosphates, fewer studies have been carried out on polyoxoanions that incorporate the pyramidal sulfite anion.[4,5] The sulfite anion has C_{3v} symmetry and contains a nonbonding, but stereochemically active pair of electrons, and their metal complexes may potentially display nonlinear optical (NLO) properties,[6] which are observed in the metal-selenites[7] and metal-iodates.[8] Herein, we report the isolation, X-ray crystal structures, and some properties of the first vanadium–sulfite species $(n\mathrm{Bu}_4\mathrm{N})_2[(\mathrm{V}^{\mathrm{IV}}\mathrm{O})_6(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\mu_3\text{-SO}_3)_4(\mathrm{H}_2\mathrm{O})_2]$ (**1**), $(\mathrm{NH}_4)_2[(\mathrm{V}^{\mathrm{IV}}\mathrm{O})_6(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\mu_3\text{-SO}_3)_4(\mathrm{H}_2\mathrm{O})_2]$ (**2**), and $(\mathrm{NH}_4)[\mathrm{V}^{\mathrm{IV}}\mathrm{O}(\mathrm{SO}_3)_{1.5}(\mathrm{H}_2\mathrm{O})]\cdot 2.5\,\mathrm{H}_2\mathrm{O}$ (**3**). Compounds **1** and **2** are polyoxovanadium(IV)–sulfite heteropolyanions that exhibit a unique structural motif with a central cubic $\{\mathrm{V}^{\mathrm{IV}}_4\mathrm{O}_2(\mathrm{OH})_2\}$ fragment and two vanadium(IV) ions located at two of the corners of the cluster. Compound **3** exhibits an open-framework structure. Open-framework materials have recently received great interest because of their applications in shape-selective catalysis, separation science, and ion-exchange.[9]

The reaction of $[\mathrm{V}^{\mathrm{IV}}\mathrm{OCl}_2(\mathrm{thf})_2]$ in an HCl solution (37% HCl in water, 1:3 v/v, approximately pH 1) with an aqueous solution (approximately pH 9) containing $\mathrm{Na}_2\mathrm{SO}_3$ and $\mathrm{Bu}_4\mathrm{NBr}$ (final pH value of the solution was approximately 2.5) resulted in the formation of compound **1** [Eq. (1)].

$$\begin{aligned}&6\,[\mathrm{V}^{\mathrm{IV}}\mathrm{OCl}_2(\mathrm{thf})_2] + 4\,\mathrm{NaSO}_3 + 2\,\mathrm{Bu}_4\mathrm{NBr} + 6\,\mathrm{H}_2\mathrm{O}\\ &\quad\rightarrow (\mathrm{Bu}_4\mathrm{N})_2[(\mathrm{V}^{\mathrm{IV}}\mathrm{O})_6\mathrm{O}_2(\mathrm{OH})_2(\mathrm{SO}_3)_4(\mathrm{H}_2\mathrm{O})_2] + 8\,\mathrm{NaCl} + 4\,\mathrm{HCl} \quad (1)\\ &\qquad + 2\,\mathrm{HBr} + 12\,\mathrm{THF}\end{aligned}$$

Compound **2** was isolated by replacing sodium sulfite and tetra-*n*-butylammonium bromide in the above synthetic procedure with ammonium sulfite. The synthesis of compound **3** was achieved by treating $\mathrm{NH}_4\mathrm{V}^{\mathrm{V}}\mathrm{O}_3$, in an HCl solution (37% HCl in water, 1:4 v/v, approximately pH 1), with $(\mathrm{NH}_4)_2\mathrm{SO}_3$ in the presence of magnesium oxide (final pH value was approximately 3) [Eq. (2)].

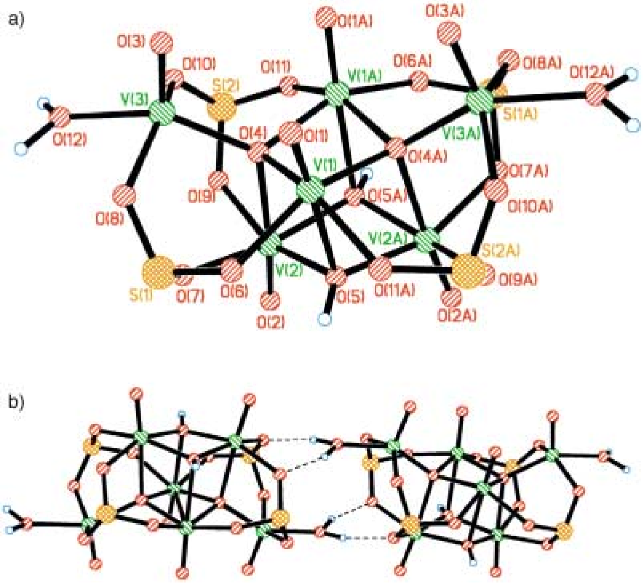

Figure 1. a) Ball-and-stick representation of **1a**. Average bond lengths (Å): V=O 1.577(6), V-O (μ_3-OH$^-$) 2.202(3), V-O (μ_4-O^{2-}) 2.073(4), V-O (μ_3-SO$_3^{2-}$) 2.024(3), V-O(H$_2$O) 2.052(2), S-O (μ_3-SO$_3^{2-}$) 1.532(8), V(1)···V(1A) 2.933(1), V(2)···V(2A) 3.185(2); b) Ball-and-stick representation of the hydrogen-bonded dimer formed between two adjacent **1a** anions.

$$\begin{aligned}&2\,\mathrm{NH}_4\mathrm{V}^{\mathrm{V}}\mathrm{O}_3 + 4\,(\mathrm{NH}_4)_2\mathrm{SO}_3\\ &\quad + 4\,\mathrm{H}_2\mathrm{O} \xrightarrow{\mathrm{MgO}} 2\,\mathrm{NH}_4[(\mathrm{V}^{\mathrm{IV}}\mathrm{O})(\mathrm{SO}_3)_{1.5}(\mathrm{H}_2\mathrm{O})]\cdot 2.5\,\mathrm{H}_2\mathrm{O}\ \mathbf{3}\\ &\quad + (\mathrm{NH}_4)_2\mathrm{SO}_4 + 6\,\mathrm{NH}_3 \qquad (2)\end{aligned}$$

In the latter reaction, absence of MgO results in the isolation of **2**. The role of MgO in the formation of **3** remains as yet unknown. Our reason for adding MgO to the reaction was to attempt to replace the V(3) and V(3A) atoms in **2** (see Figure 1) with Mg$^{\mathrm{II}}$ ions, to modify the complicated magnetic properties of compound **2**.

X-ray structural analysis of **1**[10] revealed the presence of the $[(\mathrm{V}^{\mathrm{IV}}\mathrm{O})_6(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\mu_3\text{-SO}_3)_4(\mathrm{H}_2\mathrm{O})_2]^{2-}$ anion (**1a**; Figure 1a) as well as two $\mathrm{Bu}_4\mathrm{N}^+$ counterions. The core of the hexanuclear anion **1a** consists of a distorted cubane unit, $\{\mathrm{V}^{\mathrm{IV}}_4\mathrm{O}_2(\mathrm{OH})_2\}$, which is comprised of four, triply edge-sharing

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$V^{IV}O_6$ octahedra, each having an oxo group (V=O 1.58 Å) in a position *trans* to a long V–O bond (2.36 Å); the four equatorial V–O bonds are similar in length, at approximately 2.02 Å. The two square-pyramidal O_5–V^{IV} units are coordinated to the vanadium ions of the core through one μ_4-O^{2-} and two μ_3-SO_3^{2-} bridges. The two μ_4-oxygen atoms O(4) and O(4A) connect the network of six vanadium(IV) ions and possess almost a trigonal pyramidal geometry. There are moderate-to-strong hydrogen bonds between the two hydrogen atoms of O(12)[11a] and the sulfite oxygen atoms O(7′) and O(9′), along with the symmetry-related interactions between the hydrogen atoms of O(12′) and the sulfite oxygen atoms O(7) and O(9) (Table 1). These combine to form a hydrogen-bonded dimer of two adjacent anions about a center of symmetry (Figure 1 b). There is further bonding between the hydrogen atoms of O(12A) and O(7″)/O(9″) and, by symmetry, the hydrogen atoms of O(12′A) with O(7‴)/O(9‴), etc., which links the dimeric units in 1D chains along the *a* axis. In addition, the hydroxylic hydrogen atoms H(O(5)) and H(O(5A)) form weak hydrogen bonds with the sulfite oxygen atoms O(6) and O(6A), respectively (Table 1). Although the $\{M_4(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2\}$ cubane core has been reported in the literature,[12] the connection of the $\{V^{IV}_4(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2\}$ unit with two other metals through the oxygen atoms of the core represents a novel motif, not only for vanadium species, but for any metal. In addition, there are no known examples where the $\{M_4O_4\}$ cubane core is connected to two other metals.

The structure of **2**[10] is similar to that of **1**. However, **2** crystallizes in the noncentrosymmetric space group $P2_1$, while **1** crystallizes in the centrosymmetric $I2/a$ space group. This demonstrates the crucial role of the counterion concerning the formation of noncentrosymmetric structures.[8a] The NLO properties of compound **2** were studied in aqueous solution using 1 cm- and 1 mm-thick glass cells. Under laser irradiation at 590 nm, with a 5 ns pulse duration, the NLO properties of **2** were found to be limited; experiments using lasers in the picosecond time domain are underway. Compound **3** crystallizes in the orthorhombic space group *Pbcm*[10] and exhibits a two-dimensional open-framework structure. The crystallographically unique vanadium ion of **3** resides in a distorted octahedron comprised of four equatorial sulfite oxygen atoms, as well as an oxygen atom from a water molecule and an oxo group, which occupy the axial positions (Figure 2). The 2D structure of **3** can be described as a layered net of isolated VO_6 octahedra, each sharing four corners with four adjacent SO_3 trigonal pyramids. The connectivity between the VO_6 octahedra and the SO_3 pyramids creates eight- and four-ring "windows". Each eight-ring results from four VO_6 octahedra linked by four SO_3^{2-} pyramids. In contrast, the four-rings are formed from two VO_6 octahedra that are connected through two SO_3 pyramidal units. To the best of our knowledge, the preparation of **3** represents the first example of the isolation of an open-framework compound under mild conditions.

Table 1: Hydrogen bonds for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∢ (DHA)
O12–H(12D)···O7′	0.976(5)	1.794(15)	2.702(3)	153(3)
O12–H(12E)···O9′	0.976(5)	1.916(16)	2.825(3)	154(3)
O5–H···O6	0.976(5)	2.33(4)	2.675(2)	100(2)

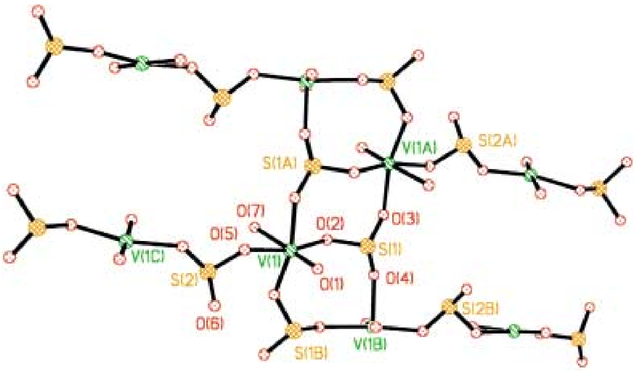

Figure 2. Structural building unit of **3** and the atomic numbering scheme. Selected interatomic distances (Å): V(1)-O(1) 1.580(7), V(1)-O(5) 1.984(6), V(1)-O(4A) 2.024(5), V(1)-O(2) 2.029(6), V(1)-O(3A) 2.057(5), V(1)-O(7) 2.280(7), S(1)-O(4) 1.548(6), S(1)-O(3) 1.548(6), S(1)-O(2) 1.551(7), S(2)-O(6) 1.506(11), S(2)-O(5) 1.549(6).

The temperature dependence of the susceptibility data for compound **1** is shown in Figure 3 in the form of χT versus T, where an overall ferromagnetic behavior is revealed. The χT value of 2.24 $cm^3 mol^{-1}$ K at room temperature is higher than the value expected for six uncorrelated $S = 1/2$ spins, and increases with decreasing temperature to a maximum value of 3.1 $cm^3 mol^{-1}$ K at 2 K.

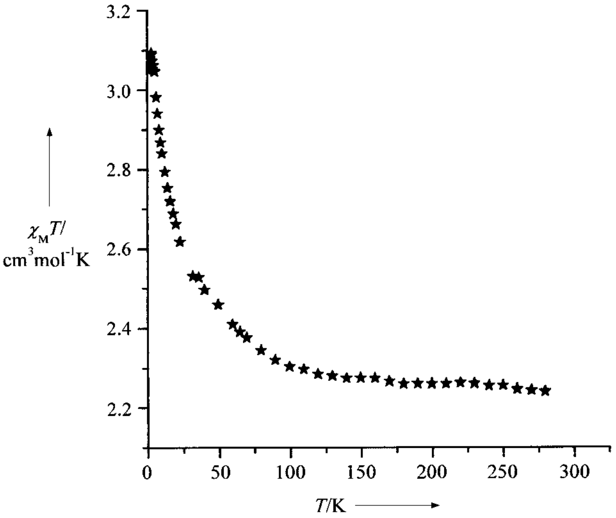

Figure 3. Temperature dependence of magnetic susceptibility given by measurements of $\chi_M T$ at 0.1 T over a temperature range of 2–300 K

Experimental Section

1: An aqueous solution (approximately 10 mL, pH 9) containing Na_2SO_3 (1.5 g, 12.0 mmol) and Bu_4NBr (7.5 g, 24.0 mmol) was added in one portion to a stirred solution of $[V^{IV}OCl_2(thf)_2]$[12] (1.5 g, 5.5 mmol) in an HCl solution (37% HCl in water, 1:4 v/v, 15 ml, pH ~ 1). Upon addition of Na_2SO_3 and Bu_4NBr the light-blue color of the solution immediately changed to dark blue and the pH value of the solution changed to approximately 2.5. Blue-green orthogonal crystals of **1** were isolated from the resulting solution after one day. Yield: 0.48 g (40 % based on V). IR: $\tilde{\nu} = 2964$ [ν(C_{But}–H)], 1000, 1021, 987, 953 [ν(V=O)], 823, 636, 508 cm^{-1} [ν(SO_3^{2-})]; UV/Vis (H_2O): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) = 238(sh, 14258) 862 (547); TGA: percentage weight loss (temperature (°C)) = 6.8 (187, assigned to H_2O), 36.5 (208, assigned to C_xH_y and NH_3), 3.6 (306, assigned to SO_x); elemental analysis calcd (%) for $C_{32}H_{78}N_2O_{24}S_4V_6$ (1308.83): C 29.37, H 6.00, N 2.14, S 9.80, V 23.35; found: C 29.68, H 6.04, N 2.17, S 9.63, V 23.50.

2: Compound **2** was prepared in 60 % yield in a similar fashion to **1**, except that $(NH_4)_2SO_3$ was used instead of Na_2SO_3 and Bu_4NBr. IR: $\tilde{\nu} = 3239$ [ν(N-H)], 1019, 989, 953 [ν(V=O)], 895, 644, 492 cm^{-1} [ν(SO_3^{2-})]; UV/Vis (H_2O): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) = 380 (1757), 266 (9034), 889 (580); TGA: percentage weight loss (temperature (°C)): 6.2 (170, assigned to H_2O), 3.9 (352, assigned to NH_3), 24.1 (501, assigned to SO_x); elemental analysis calcd (%) for $H_{14}N_2O_{24}S_4V_6$ (860.01): H 1.64, N 3.26, S 14.92, V 35.54; found: H 1.75, N 3.10, S 15.10, V 35.85.

3: Solid MgO (7.0 g, 174 mmol) was added in one portion to a stirred solution of NH_4VO_3 (1.5 g, 12.8 mmol) in diluted HCl (37 % HCl in water, 1:4 v/v, 20 mL, pH ~ 1.5). Upon addition of MgO, the yellow color of the solution did not change. Solid $(NH_4)_2SO_3$ (1.5 g, 15.3 mmol) was then added to the solution, the color of which immediately turned blue, and the pH value changed to approximately 3.0. Blue hexagonal crystals of **3** were precipitated from the solution after 2 days. Yield: 2.06 g (60 % based on V). IR: $\tilde{\nu} = 3262$ [ν(NH_4^+)], 1019, 987, 953 [ν(V=O)], 904 cm^{-1} [ν(SO_3^{2-})]; UV/Vis (H_2O): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) = 896 (2230), 235(sh, 6750); TGA: percentage weight loss (temperature (°C)): 26.8 (270, assigned to H_2O), 6.3 (361, assigned to NH_3) 35.8 (519.9, assigned to SO_2); elemental analysis calcd (%) for $H_{11}NO_9S_{1.5}V$ (268.13): H 4.13, N 5.22, S 17.94, V 19.00; found: H 4.20, N 5.10, S 18.05, V 18.80.

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[10] Crystal data for **1**: $C_{32}H_{78}N_2O_{24}S_4V_6$, $M_w = 1308.83$, monoclinic, space group $I2/a$, $a = 20.48910(10)$, $b = 16.6679(4)$, $c = 18.0218(3)$ Å, $\beta = 111.3460(10)°$, $V = 5732.42(17)$ Å^3, $Z = 4$, $\rho_{calc} = 1.517$ Mg m^{-3}, $T = 293(2)$ K; $R1$(final) = 0.0274, $wR2 = 0.0693$. Crystal data for **2**: $H_{14}N_2O_{24}S_4V_6$, $M_W = 860.01$, monoclinic, space group $P2_1$, $a = 7.596(3)$, $b = 20.033(9)$, $c = 7.624(3)$ Å, $\beta = 91.157(8)°$, $V = 1159.9(9)$ Å^3, $Z = 2$, $\rho_{calc} = 2.463$ Mg m^{-3}, $T = 293(2)$ K; $R1$(final) = 0.1226, $wR2 = 0.3021$. The structure of **2** was determined using different crystals under a variety of conditions (including two determinations at 125 K); the reported data are the best that were obtained. Crystal data for **3**: $H_{11}NO_9S_{1.5}V$, $M = 268.13$, orthorhombic, space group *Pbcm*, $a = 7.0680(17)$, $b = 12.536(3)$, $c = 19.968(5)$, $V = 1769.2(7)$ Å^3, $Z = 8$, $\rho_{calc} = 2.013$ Mg m^{-3}, $T = 293(2)$ K. $R1$(final) = 0.0586, $wR2 = 0.1140$. CCDC-179446 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). Further details on the crystal structure investigations for **2** and **3** 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 numbers CSD-412712 and -412713.

[11] a) Bond valence sum (BVS) calculations for compound **1**: BVS calculations for O(5) and O(12) gave values of 1.24 and 0.47, respectively, while calculations for the crystallographically independent vanadium and sulfur ions gave values very close to 4. b) BVS calculations for compound **3**: BVS calculations for O(7) and O(1) gave values of 0.23 and 1.2, respectively, while calculations for the crystallographically independent vanadium and sulfur ions gave values very close to 4 [I. D. Brown in *Structure and Bonding in Crystals, Vol. II* (Ed.: M. O'Keefe, A. Navrotdsky), Academic Press, New York, **1981**, p. 1–30].

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