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Revue / Account

A novel compound with a 1D network structure constructed by $[(V^{IV}O)_6(\mu_4-O)_2(\mu_3-OH)_2(\mu_3-SO_3)_4]^{2-}/SO_3^{2-}$ and 4,4'-bipyridine components: its synthesis, characterization, and magnetic behavior

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Dedicated to Professor Francis Secheresse on the occasion of his 60th birthday

Abstract

The organically templated compound $(NH_4)_3(4,4'\text{-Hbpy})[(V^{IV}O)_6(\mu_4-O)_2(\mu_3-OH)_2(\mu_3-SO_3)_4(\mu-SO_3)] \cdot 15/2 H_2O$ **1** is the first example of an extended structure in which a polyoxometalate anion, $[H_2V_6^{IV}S_4^{IV}O_{22}]^{2-}$, is linked by the pyramidal μ_2 -bridging sulfite group forming a linear polymeric $\{V_6\}_n$ chain. Two such chains are linked into a 'double-rung ladder' assembly via two different hydrogen bonds provided by 4,4'-Hbpy⁺ cations. **To cite this article:** H.N. Miras et al., C. R. Chimie 8 (2005).

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Résumé

Le composé $(NH_4)_3(4,4'\text{-Hbpy})[(V^{IV}O)_6(\mu_4-O)_2(\mu_3-OH)_2(\mu_3-SO_3)_4(\mu-SO_3)] \cdot 15/2 H_2O$ **1** synthétisé grâce à un template organique est le premier exemple de structure étendue dans laquelle un polyanion, $[H_2V_6^{IV}S_4^{IV}O_{22}]^{2-}$, est relié par des groupements sulfite pyramidaux μ_2 -pontants, pour former une chaîne polymérique $\{V_6\}_n$. Les chaînes s'assemblent deux à deux dans une « échelle à double barreau » par l'intermédiaire de deux sortes de liaisons hydrogène à partir des cations 4,4'-Hbpy⁺. **Pour citer cet article :** H.N. Miras et al., C. R. Chimie 8 (2005).

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Keywords: Magnetism polyoxometalates; Sulfite; Vanadium

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Self-assembly of inorganic precursors in a quest for supramolecular chemistry is one of the highly recognized areas of chemical research [1–4]. The significant contemporary interest in polyoxovanadium-based solid materials reflects their diverse applications in the areas such as catalysis [1,2], materials science [2g], magnetism [1,5] and non-linear optics [1,2]. In studies of these materials, an astonishing variety of novel phases arises from the combination of vanadium progenitors and organic molecules [6]. Such structural variety arises from the versatility of vanadium in terms of its variable oxidation state (III, IV and V) and coordination geometry (tetrahedral, square pyramidal and octahedral), combined with the structure directing and stabilizing effect of the organic molecules. The combination of vanadium POMs with organic molecules adds complexity to the structures and promotes the adjustment of the physicochemical properties of these materials. Moreover, investigations on POM-organic/inorganic systems well characterized at molecular level, might provide structural and spectroscopic models [7] for heterogeneous metal oxide-supported catalysts. In comparison to the extensive work on polyoxometal-phosphates [8] only a very few polyoxometal-sulfites have been reported [9]. Being successful in synthesizing and characterizing polyoxometal-sulfites, we decided to prepare organic/POM-sulfite species. Herein, we report the synthesis, structural and physicochemical characterization, of the first organic/inorganic polyoxometal-sulfite compound $(\text{NH}_4)_3(4,4'\text{-Hbpy})[(\text{V}^{\text{IV}}\text{O})_6(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\mu_3\text{-SO}_3)_4(\mu\text{-SO}_3)] \cdot 15/2 \text{H}_2\text{O}$ **1**.

Solid $(\text{NH}_4)_2\text{SO}_3$ (6.00 g, 61.2 mmol) was added in one portion to a stirred solution of $\text{NH}_4\text{V}^{\text{V}}\text{O}_3$ (0.60 g, 5.1 mmol, pH 0) in concentrated (37%) $\text{HCl}/\text{H}_2\text{O}$ (1:4 v/v, 20 ml). Upon addition of $(\text{NH}_4)_2\text{SO}_3$ the light-yellow color of the solution changed to blue–green, and its pH value was ca. 4. After stirring the solution for ~15 min, it was filtered and an ethanolic solution (6 ml) containing 4,4'-bpy (0.40 g, 2.5 mmol) was layered on it. A layer of diethyl ether was placed between these two layers. Green hexagonal crystals of **1**, suitable for X-ray crystal structure analysis¹, were obtained after

3 days. Yield 0.48 g (31%) based on vanadium. Compound **1**² is indefinitely stable in air.

The structure of compound **1** consists of a one-dimensional extended network constructed by vanadium building-blocks, $[\text{H}_2\text{V}_6^{\text{IV}}\text{S}_4^{\text{IV}}\text{O}_{22}]^{2-}/\text{SO}_3^{2-}$, protonated bipyridine (4,4'-Hbpy⁺) as well as ammonium cations and interstitial water molecules. Neighboring $[\text{H}_2\text{V}_6^{\text{IV}}\text{S}_4^{\text{IV}}\text{O}_{22}]^{2-}$ shells are linked together by the pyramidal μ_2 -(O,O) bridging sulfite groups to form infinite chains running along [001]. Two such chains are linked into a 'double-rung ladder' assembly via two different hydrogen bonds provided by singly protonated bipyridine cations (Fig. 1). The principal interatomic distances and selected bond angles for **1** are reported in Table 1. The 4,4'-Hbpy⁺ is nearly planar with the two pyridyl rings twisted by 11.6(4)°. One strong hydrogen bond is formed between H(9) [of the triply-bridging O(9) hydroxo ligand] and the N(1) atom of 4,4'-Hbpy⁺ [O(9)⋯N(1), 2.661(4) Å, 179.0°]. Another hydrogen bond is formed between H(2) of 4,4'-Hbpy⁺ and O(4) {oxo-ligand of the vanadium cluster; [N(2)⋯O(4), 2.731(6) Å, 174.8°]}. Packing between ladder ribbons is achieved by an extensive hydrogen-bonding system in which all ammonium cations and water molecules are involved. The structure of the vanadosulfite building block (Fig. 2), $[\text{H}_2\text{V}_6^{\text{IV}}\text{S}_4^{\text{IV}}\text{O}_{22}]^{2-}$, is essentially identical to that previously reported [9b]. The cluster consists of a distorted cubane unit, $[\text{H}_2\text{V}_4\text{O}_4]$, which is connected to two outer distorted square-pyramidal vanadium(IV) atoms through two μ_4 -O²⁻ bridges and four μ_3 -SO₃²⁻ bridges as well. Bond valence sum (BVS) [10] calculations (Table 2) for the crystallographically independent vanadium atoms gave values in the range of 3.94–4.04 suggesting that all vanadium atoms are in the oxidation state of IV. BVS calculation [10] for the

¹ Elemental analysis calcd. (%) for $\text{C}_{10}\text{H}_{38}\text{N}_5\text{O}_{32.5}\text{S}_5\text{V}_6$ (1214.39): C: 9.88, H: 3.12, N: 5.76, S: 13.17, V: 25.17; found: C: 9.81, H: 3.04, N: 5.63, S: 12.98, V: 25.01.

² X-Ray crystal structure analysis for **1**: $(\text{NH}_4)_3(4,4'\text{-bipyH})[(\text{V}^{\text{IV}}\text{O})_6(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\mu_3\text{-SO}_3)_4(\mu\text{-SO}_3)] \cdot 15/2 \text{H}_2\text{O}$: $\text{C}_{10}\text{H}_{38}\text{N}_5\text{O}_{32.5}\text{S}_5\text{V}_6$, $M_r = 1214.39$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.739(2)$ Å, $b = 11.002(2)$ Å, $c = 18.028(4)$ Å, $\alpha = 86.972(4)^\circ$, $\beta = 78.215(4)^\circ$, $\gamma = 69.160(4)^\circ$, $V = 1948.1(7)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 2.070$ Mg m⁻³, $T = 299(2)$ K, $R1 = 0.0481$, $wR2 = 0.1142$, index ranges = $-14 \leq h \leq 13$, $-9 \leq k \leq 14$, $-23 \leq l \leq 16$; intensity data collection was carried out on a green crystal of $0.07 \times 0.05 \times 0.03$ mm and refined by full-matrix least-squares, based on F^2 . CCDC reference number 255738. See <http://www.rsc.org/suppdata/dt/b1/b108430p/> for crystallographic data in CIF or other electronic format.

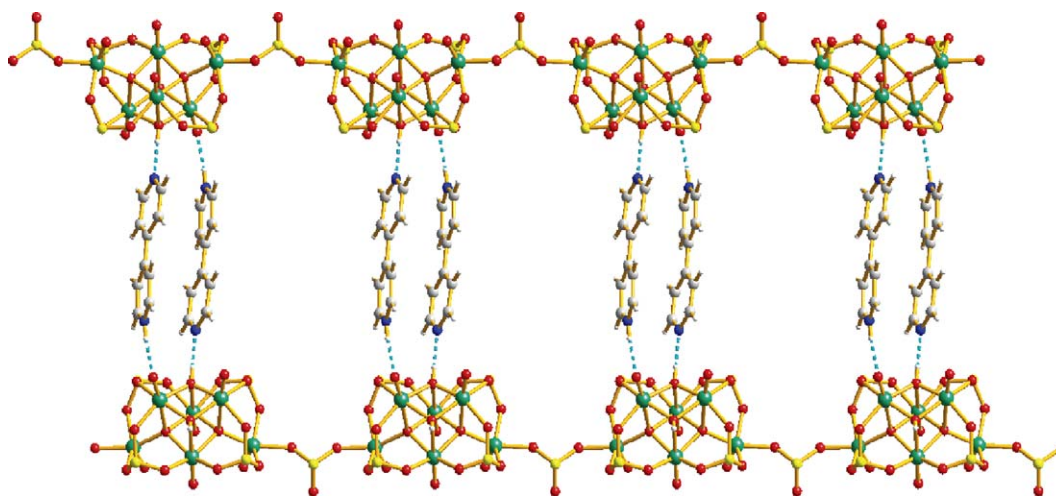


Fig. 1. Ball-and-stick representation of compound 1.

triply bridging oxygen atoms [O(9) and O(10)], gave values of 1.06 and 1.05, respectively, indicating single protonation according to elemental analysis and charge balance, while the sulfur atoms gave values very close to 4.

The infrared spectrum of **1** exhibits bands at 3504s (br) [$\nu(\text{O-H})$ from H_2O], 3127s (br) [$\nu(\text{N-H})$ from NH_4^+], 1637m (br) [$\delta(\text{H}_2\text{O})$], 1607m, 1560w, 1211w [$\nu(4,4'\text{-Hbpy}^+)$], 1401s [$\delta(\text{NH}_4^+)$], 1028sh, 922s, 874s, 834s, 814m and 568s cm^{-1} [$\nu(\text{SO}_3^{2-})$] [11], 979s and 971sh cm^{-1} [$\nu(\text{V=O})$], respectively. The electronic spectrum of **1** in aqueous solution consists of a band in the visible and a peak in the ultraviolet region, namely, $\lambda/\text{nm}(\epsilon/\text{M}^{-1} \text{cm}^{-1})$: 889(sh) (1261), 251 (18,440). The UV–Vis solid state reflectance of compound **1**, revealed a band at 251 nm, thus indicating that **1** loses its integrity in aqueous solution.

The experimental magnetic data for **1** are plotted as $\chi_M T$ vs. T in Fig. 3A. The $\chi_M T$ value decreases from 1.74 $\text{emu mol}^{-1} \text{K}$ at 300 K, which is significantly smaller with the expected value of 2.25 $\text{emu mol}^{-1} \text{K}$ for six non-interacting V^{IV} centers ($S = 1/2$), to 1.53 $\text{emu mol}^{-1} \text{K}$ at 78 K and then increases abruptly to the value of 1.70 $\text{emu mol}^{-1} \text{K}$ at 5.8 K and then drastically decreases to the value of 1.48 at 1.8 K. The behavior of $\chi_M T$ suggests the existence of very strong antiferromagnetic interactions along with ferromagnetic exchange interactions within the molecule. The Hamiltonian formalism used to fit the experimental data for this V^{IV}_6 system (Scheme 1) is given by Eq. 1.

$$\begin{aligned}
 H = & J_1(S_1 S_2) + J_2(S_3 S_4) \\
 & + J_3[S_1(S_3 + S_4) + S_2(S_3 + S_4)] \\
 & + J_4[S_5(S_3 + S_4 + S_2) + S_6(S_3 + S_4 + S_1)]
 \end{aligned} \quad (1)$$

Using Eq. (1) a very good fit (solid line in Fig. 3A) was obtained. The resulting parameters are, $J_1 = -1.27 \text{ cm}^{-1}$, $J_2 = 112.3 \text{ cm}^{-1}$, $J_3 = 51.1 \text{ cm}^{-1}$, $J_4 = 0.21 \text{ cm}^{-1}$, $g = 1.99$. This fit reveals the existence of one small ferromagnetic exchange parameter within the V^{IV}_6 cluster that is between V1 and V2 ions (Scheme 1) [$\text{V}\cdots\text{V} = 3.131(1) \text{ \AA}$, average $\text{V-O-V} = 103.6(1)^\circ$] although an antiferromagnetic one is expected. The reason for this discrepancy comes from the two large antiferromagnetic interactions that influence the behavior of the system and the existence of many triangles in it leading to frustration effects. An important result is the significant antiferromagnetic interaction between the V3 and V4 ions [$\text{V}\cdots\text{V} = 2.890(1) \text{ \AA}$, average $\text{V-O-V} = 92.9(1)^\circ$] which is mainly due to the very small distance (almost a metallic bond) and for this reason there is a direct exchange interaction instead of a superexchange one. The energy diagram of the system reveals that the ground state is a $S_T = 0$ and two different $S_T = 1$ excited states are at ca. 0.5 cm^{-1} and 0.9 cm^{-1} , respectively, while the $S = 2$ excited state is at 1.4 cm^{-1} . In order to verify the above fitting parameters, variable field magnetization data were collected at two different temperatures 2.5 and 4.5 K. The data are plotted as $M/N\mu_B$ vs. H/T in Fig. 3B

Table 1
Principal interatomic distances (Å) and selected bond angles (°) for the compound **1**

Bond lengths (Å)					
V(1)–O(1)	1.607(3)	V(3)–O(3)	1.596(3)	V(5)–O(5)	1.594(3)
V(1)–O(7)	1.989(3)	V(3)–O(9)	1.984(3)	V(5)–O(19)	1.971(3)
V(1)–O(8)	1.990(3)	V(3)–O(10)	1.999(3)	V(5)–O(13)	1.974(3)
V(1)–O(14)	2.034(3)	V(3)–O(18)	2.031(3)	V(5)–O(23)	1.976(3)
V(1)–O(11)	2.036(3)	V(3)–O(12)	2.046(3)	V(5)–O(7)	2.002(3)
V(1)–O(9)	2.260(3)	V(3)–O(7)	2.255(3)	V(6)–O(6)	1.591(4)
V(2)–O(2)	1.599(3)	V(4)–O(4)	1.607(3)	V(6)–O(24)	1.972(3)
V(2)–O(8)	1.996(3)	V(4)–O(10)	1.988(3)	V(6)–O(22)	1.973(3)
V(2)–O(7)	1.998(3)	V(4)–O(9)	1.993(3)	V(6)–O(16)	1.991(3)
V(2)–O(17)	2.025(3)	V(4)–O(21)	2.011(3)	V(6)–O(8)	2.005(3)
V(2)–O(20)	2.030(3)	V(4)–O(15)	2.022(3)	V(1)···V(2)	2.8894(11)
V(2)–O(10)	2.302(3)	V(4)–O(8)	2.240(3)	V(3)···V(4)	3.1304(11)
				V(3)···V(5)	3.6261(12)
				V(4)···V(6)	3.6001(13)
Bond angles (°)					
O(1)–V(1)–O(7)	103.33(13)	O(20)–V(2)–O(10)	76.84(11)	O(5)–V(5)–O(13)	106.45(16)
O(1)–V(1)–O(8)	103.91(14)				
O(7)–V(1)–O(8)	85.58(11)	O(2)–V(2)–V(1)	99.84(12)	O(19)–V(5)–O(13)	142.93(14)
O(1)–V(1)–O(14)	100.00(14)	O(8)–V(2)–V(1)	43.47(8)	O(5)–V(5)–O(23)	101.58(17)
O(7)–V(1)–O(14)	156.55(12)	O(7)–V(2)–V(1)	43.43(8)	O(19)–V(5)–O(23)	84.69(13)
O(8)–V(1)–O(14)	91.09(11)	O(17)–V(2)–V(1)	132.74(9)	O(13)–V(5)–O(23)	80.56(13)
O(1)–V(1)–O(11)	99.24(14)	O(20)–V(2)–V(1)	133.33(8)	O(5)–V(5)–O(7)	102.08(14)
O(7)–V(1)–O(11)	91.28(11)	O(10)–V(2)–V(1)	83.92(7)	O(19)–V(5)–O(7)	90.01(12)
O(8)–V(1)–O(11)	156.74(12)	O(3)–V(3)–O(9)	102.07(14)	O(13)–V(5)–O(7)	90.05(12)
O(14)–V(1)–O(11)	82.69(11)	O(3)–V(3)–O(10)	104.07(15)	O(23)–V(5)–O(7)	156.17(15)
O(1)–V(1)–O(9)	176.56(13)	O(9)–V(3)–O(10)	74.96(11)	O(6)–V(6)–O(24)	103.55(19)
O(7)–V(1)–O(9)	78.92(10)	O(3)–V(3)–O(18)	98.10(15)	O(6)–V(6)–O(22)	107.69(17)
O(8)–V(1)–O(9)	78.76(11)	O(9)–V(3)–O(18)	157.38(12)	O(24)–V(6)–O(22)	86.21(14)
O(14)–V(1)–O(9)	77.67(11)	O(10)–V(3)–O(18)	90.34(12)	O(6)–V(6)–O(16)	106.52(18)
O(11)–V(1)–O(9)	78.01(11)	O(3)–V(3)–O(12)	95.75(16)	O(24)–V(6)–O(16)	78.60(14)
O(1)–V(1)–V(2)	99.08(11)	O(9)–V(3)–O(12)	90.77(12)	O(22)–V(6)–O(16)	144.95(15)
O(7)–V(1)–V(2)	43.69(8)	O(10)–V(3)–O(12)	157.52(12)	O(6)–V(6)–O(8)	102.70(15)
O(8)–V(1)–V(2)	43.62(8)	O(18)–V(3)–O(12)	97.35(13)	O(24)–V(6)–O(8)	153.38(17)
O(14)–V(1)–V(2)	134.00(9)	O(3)–V(3)–O(7)	176.30(15)	O(22)–V(6)–O(8)	90.08(12)
O(11)–V(1)–V(2)	134.27(8)	O(9)–V(3)–O(7)	79.12(10)	O(16)–V(6)–O(8)	89.75(12)
O(9)–V(1)–V(2)	84.35(7)	O(10)–V(3)–O(7)	79.60(11)	V(1)–O(7)–V(2)	92.89(11)
O(2)–V(2)–O(8)	104.06(14)	O(18)–V(3)–O(7)	81.40(11)	V(1)–O(7)–V(5)	120.77(13)
O(2)–V(2)–O(7)	104.27(14)	O(12)–V(3)–O(7)	80.71(11)	V(2)–O(7)–V(5)	120.48(13)
O(8)–V(2)–O(7)	85.17(11)	O(4)–V(4)–O(10)	103.36(15)	V(1)–O(7)–V(3)	100.28(11)
O(2)–V(2)–O(17)	100.47(14)	O(4)–V(4)–O(9)	104.05(15)	V(2)–O(7)–V(3)	101.16(11)
O(8)–V(2)–O(17)	155.43(12)	O(10)–V(4)–O(9)	75.02(11)	V(5)–O(7)–V(3)	116.67(12)
O(7)–V(2)–O(17)	90.16(11)	O(4)–V(4)–O(21)	97.62(15)	V(1)–O(8)–V(2)	92.91(11)
O(2)–V(2)–O(20)	100.33(14)	O(10)–V(4)–O(21)	92.18(12)	V(1)–O(8)–V(6)	120.99(14)
O(8)–V(2)–O(20)	90.76(11)	O(9)–V(4)–O(21)	156.82(12)	V(2)–O(8)–V(6)	120.96(14)
O(7)–V(2)–O(20)	155.32(12)	O(4)–V(4)–O(15)	94.21(15)	V(1)–O(8)–V(4)	100.78(12)
O(17)–V(2)–O(20)	83.48(11)	O(10)–V(4)–O(15)	158.62(12)	V(2)–O(8)–V(4)	100.79(12)
O(2)–V(2)–O(10)	176.23(13)	O(9)–V(4)–O(15)	89.07(12)	V(6)–O(8)–V(4)	115.90(12)
O(8)–V(2)–O(10)	78.60(11)	O(21)–V(4)–O(15)	97.54(14)	V(3)–O(9)–V(4)	103.85(12)

(continued on next page)

Table 1
(continued)

O(7)–V(2)–O(10)	78.49(10)	O(4)–V(4)–O(8)	175.57(14)	V(3)–O(9)–V(1)	100.28(11)
O(17)–V(2)–O(10)	76.83(11)	O(10)–V(4)–O(8)	80.29(11)	V(4)–O(9)–V(1)	100.02(12)
		O(9)–V(4)–O(8)	79.21(11)	V(4)–O(10)–V(3)	103.47(12)
		O(21)–V(4)–O(8)	79.62(12)	V(4)–O(10)–V(2)	98.95(12)
		O(15)–V(4)–O(8)	82.79(12)	V(3)–O(10)–V(2)	99.57(11)
		O(5)–V(5)–O(19)	109.75(16)		

(where N is the Avogadro's number and μ_B is the Bohr magneton). The same magnetic model was used to simulate the data and the results (solid lines in Fig. 3B) are in perfect agreement with the experimental data at 4.5 K while there is a discrepancy with the data at 2.5 K possibly due to the 1-D character of the system.

In conclusion, the successful isolation of a novel one-dimensional species $(\text{NH}_4)_3(4,4'\text{-Hbpy})[(\text{V}^{\text{IV}}\text{O})_6(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\mu_3\text{-SO}_3)_4(\mu\text{-SO}_3)] \cdot 15/2 \text{H}_2\text{O}$ **1**, provides a novel example of assembling vanadosulfite with sulfite anion through the structure-control effect of 4,4'-

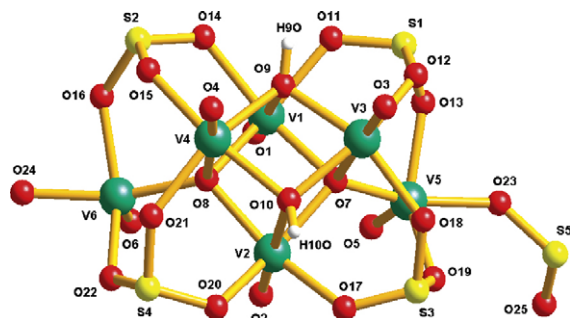


Fig. 2. Ball and stick representation of the vanadium building block, $[\text{H}_2\text{V}_6^{\text{IV}}\text{S}_4^{\text{IV}}\text{O}_{22}]^{2-}$ in **1**. Average bond lengths (\AA): V=O 1.599(3), V–O ($\mu_3\text{-O}$) 2.096(3), V–O ($\mu_4\text{-O}$) 2.107(3), S–O ($\mu_3\text{-SO}_3^{2-}$) 1.532(3), S=O 1.446(4).

Table 2

Bond valance sum calculations for the vanadium, sulfur and oxygen atoms for the compound **1**

Atom	BVS	Atom	BVS	Atom	BVS
V(1)	3.99	O(7)	1.89	O(19)	1.54
V(2)	4.00	O(8)	1.59	O(20)	1.55
V(3)	4.03	O(9)	1.06	O(21)	1.54
V(4)	4.04	O(10)	1.07	O(22)	1.55
V(5)	3.95	O(11)	1.63	O(23)	1.62
V(6)	3.94	O(12)	1.75	O(24)	1.74
O(1)	1.65	O(13)	1.55	O(25)	1.48
O(2)	1.69	O(14)	1.54	S(1)	3.97
O(3)	1.71	O(15)	1.54	S(2)	3.95
O(4)	1.65	O(16)	1.55	S(3)	3.97
O(5)	1.72	O(17)	1.54	S(4)	3.87
O(6)	1.74	O(18)	1.55	S(5)	3.96

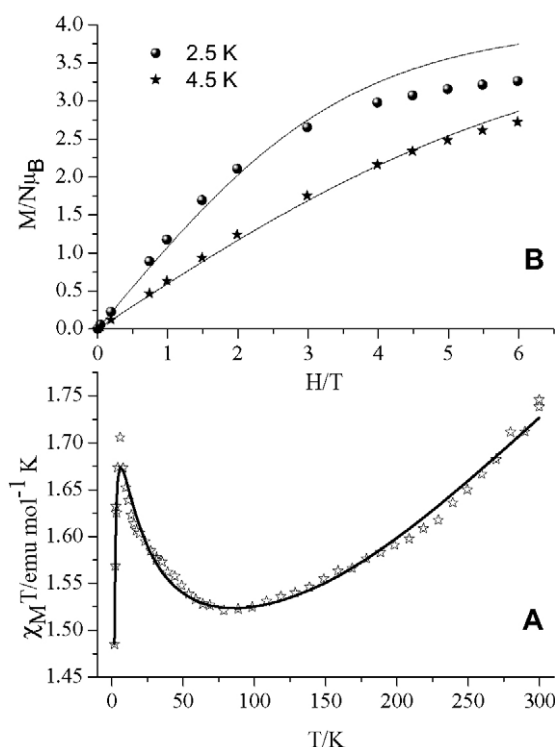
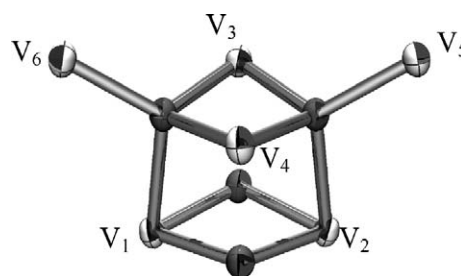


Fig. 3. A) Temperature dependence of the susceptibility data, in the form of $\chi_M T$ vs. T for **1**. The solid line represents the fitting results according to equation 1; B) magnetization data for **1** at 2.5 and 4.5 K.



Scheme 1.

Hbpy⁺ cation. In addition, compound **1** is the first organic/inorganic polyoxometal-sulfite species in which the 4,4'-Hbpy⁺ ligand is only involved in hydrogen-bonding. Variable temperature magnetic susceptibility measurements revealed an overall antiferromagnetic behavior for **1**, in marked contrast to the ferromagnetic behavior for the previously described hexanuclear species [H₂V₆^{IV}S₄^{IV}O₂₂]²⁻ [9b].

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