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Antimonato Polyoxovanadate Based Three-Dimensional Framework Exhibiting Ferromagnetic Exchange Interactions: Synthesis, Structural Characterization, and Magnetic Investigation of $\{[Fe(C_6H_{14}N_2)_2]_3[V_{15}Sb_6O_{42}(H_2O)]\}\cdot 8H_2O$

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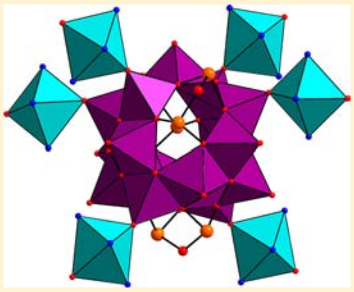
Ⓢ *Supporting Information*

ABSTRACT: The new polyoxovanadate $\{[Fe(C_6H_{14}N_2)_2]_3[V_{15}Sb_6O_{42}(H_2O)]\}\cdot 8H_2O$ (**1**) was obtained under solvothermal conditions using the amine that acts at the same time as the ligand, solvent, and reducing agent. The central structural motif of **1**, $[V_{15}Sb_6O_{42}(H_2O)]^{6-}$, is related to the $\{V_{18}O_{42}\}$-archetype cluster by replacing three VO_5 square pyramids with three $O_2Sb{-}O{-}SbO_2$ moieties. Every $[V_{15}Sb_6O_{42}(H_2O)]^{6-}$ cluster anion is expanded by six FeN_4O_2 octahedra, thus generating a rare three-dimensional network with differently sized pores hosting the crystal water molecules. In **1**, two $[V_{15}Sb_6O_{42}(H_2O)]^{6-}$ cluster anions with different orientations coexist. According to bond-valence-sum calculations, the anionic cluster can be formulated as $[V^{IV}{}_{15}Sb^{III}{}_6O_{42}(H_2O)]^{6-}$, i.e., in line with the valence states of all other known $\{V_{15}Sb_6\}$ clusters. The optical band gap of **1** was determined as 2.47 eV. Investigation of the magnetic behavior indicates dominating ferromagnetic exchange interactions between the V^{4+} centers of the cluster and the Fe^{2+} d^6 cations.



■ INTRODUCTION

A milestone in the chemistry of polyoxovanadates (POVs) was the discovery of nanoscale magnetism of the arsenato polyoxovanadate compound $K_6[V_{15}As_6O_{42}(H_2O)]\cdot 8H_2O$.[1] Since then, the compound was intensively studied, and the results are documented in more than 60 publications.[2−11] The remarkable magnetic properties of $[V_{15}As_6O_{42}]^{6-}$ are caused by layers of different magnetization including a V^{IV} triangle displaying magnetic frustration, and the magnetic ground state is characterized by $S = {}^1/_2$. Similar POVs are of interest for their partially delocalized electronic charges, in particular with a V 3d character. Such charge delocalization in mixed-valence clusters can cause a strong increase of the spin coupling.[10] Because of these properties, the $\{V_{18}O_{42}\}$-type clusters were described as the most interesting ones[9] especially because two different types of symmetry (T_d and D_{4d}) accompanied by large electron populations exist for $\{V_{18}O_{42}\}$.[11]

Motivated by these interesting properties of POVs, intensive research work aims to interfere with the self-assembly of POVs, especially in order to interlink the cluster anions to extended frameworks or to augment the cluster structures with other spin centers. One current area of research thus targets the assembly, interconnection, and extension of arsenato-based POV clusters using transition-metal complexes as structural modifiers. Such structural modifications promise a new generation of structure types characterized by physical properties that significantly differ from those of the archetype phases. The interconnection of arsenato polyoxovanadate cluster anions by transition-metal complexes in most cases results in extended network structures, exemplified by a range of compounds based on spherical $[V_{18-x}As_{2x}O_{42}]\cdot nH_2O$ ($x = 2{-}4$) clusters.[12a−k] One example for the coexistence of a discrete cluster anion and a Zn^{2+} complex is given by $[Zn(2,2'\text{-bpy})_3][V_{14}As_8O_{42}(H_2O)]$ (2,2′-bpy = 2,2′-bipyridine), where the cluster anions are surrounded by two $[Zn(2,2'\text{-bpy})_3]^{2+}$ complexes and the interactions between the two constituents are only electrostatic.[12a] However, the interaction of a $[V_{14}As_8O_{42}(H_2O)]^{4-}$ cluster with a $[Zn(2,2'\text{-bpy})(\text{dien})]^{2+}$ complex (dien = diethylentriamine) can also occur via hydrogen bonding between the N−H atoms of the amine and terminal O atoms of the cluster anion. Similar hydrogen-bonding interactions were reported for $[Zn(H_2O)_4)_2][H_2V_{15}As_6O_{42}(H_2O)]$.[12b] A unique structure was observed for $[\{Ni(en)_2\}_4(4,4'\text{-bpy})_4\{Ni(H_2O)_2\}]_2[V_{14}As_8O_{42}(NO_3)]_4\cdot 16H_2O$ (4,4′-bpy = 4,4′-bipyridine).[12c] In this inorganic−organic hybrid material, the clusters are extended by two $[\{Ni(en)_2\}_4(4,4'\text{-bpy})_4\{Ni(H_2O)_2\}]^{10+}$ (en = ethylenediamine) fragments linked to four further $[V_{14}As_8O_{42}(NO_3)]^{5-}$ anions. This coordination mode leads to the formation of a closed boxlike structure, in which the POV functions as a linker between Ni^{2+} cations. Examples for one-dimensional structures with cluster anions being linked by Ni^{2+}-centered complexes have been reported by several working groups,[12c,d] and one-dimensional networks were also realized using $[Cu(en)_2]^{2+}$,[12e] $[Zn_2(\text{dien})_3(H_2O)_2]^{4+}$,[12d] $[Zn_2(\text{dien})_3]^{4+}$,[12f] $[Zn_2(2,2'\text{-bpy})_2]^{2+}$,[12g] and [Cd(2,2′-

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bpy$)_3]^{2+}$[12g] complexes as bridging molecules. In these compounds, the transition-metal complexes connect two terminal O atoms of the clusters, leading to distorted octahedral or tetrahedral geometries around the transition-metal cations. Two-dimensional networks with $[Ni(en)_2]^{2+}$ ions as bridging molecules have been reported by Cui et al.[12h] and Zheng et al.,[12g] where terminal O atoms of the $[V_{14}As_8O_{42}(X)]^{6-}$ clusters (X = SO_4, HPO_4) are bound to the Ni^{2+} complexes, leading to a distorted octahedral geometry around Ni^{2+}. Such two-dimensional networks could also be synthesized with $[Cu(en)_2]^{2+}$,[12i] and $[Co(enMe)_2]^{2+}$ (enMe = methylethylenediamine),[12d] as well as $[Ln(H_2O)_6]^{3+}$ (Ln = La, Sm, Ce).[12j] Finally, a three-dimensional network was obtained by covalent linkage between tetradentate-acting $[V_{14}As_8O_{42}]^{4-}$ clusters and cationic ladder-like double chains of $[Cu(bbi)]_n$ [bbi = 1,1′-(1,4-butanediyl)bis(imidazole)].[12k]

The characterization of the magnetic properties of the arsenato polyoxovanadate clusters mentioned above indicates strong antiferromagnetic coupling of magnetic centers within the cluster anion, and no significant magnetic interaction between the spins of the transition-metal cations in the linking complexes and the spin-$^1/_2$ vanadyl groups of the clusters is observed.

The analogous antimonato and germanato polyoxovanadate chemistry is much less developed, and during the past few years, we hydrothermally synthesized a number of new modified inorganic−organic hybrid materials[13b,c,14,15] based on the $\{V_{18}O_{42}\}$ archetype cluster where VO_5 square pyramids are successively replaced by Sb_2O_5 or Ge_2O_7, yielding structural motifs like $\{V_{16}O_{42}\}$, $\{V_{15}O_{42}\}$, and $\{V_{14}O_{42}\}$. For example, in the two compounds $(Co(N_3C_5H_{15})_2)_2[\{Co(N_3C_5H_{15})_2\}V_{15}Sb_6O_{42}(H_2O)]\cdot5H_2O$ and $(Ni(N_3C_5H_{15})_2)_2$ $[\{Ni(N_3C_5H_{15})_2\}V_{15}Sb_6O_{42}(H_2O)]\cdot8H_2O$, the spherical cluster anions are expanded by Co^{2+} and Ni^{2+} complexes, respectively,[15e] while in $[V_{14}Sb_8(C_6H_{15}N_3)_4O_{42}(H_2O)]\cdot4H_2O$, protonated amine molecules are bonded to Sb atoms of the cluster, yielding a charge-neutral molecule.[15b]

The aims of our ongoing work are the synthesis and characterization of new antimonato polyoxovanadate architectures and the interconnection of Sb-modified POVs by in situ formed transition-metal complexes to generate structures with higher dimensionality. In this work, we present the first example of an antimonato polyoxovanadate cluster being joined by FeN_4O_2 octahedra to form a three-dimensional network.

■ RESULTS AND DISCUSSION

Crystal Structure. Compound $\{[Fe(C_6H_{14}N_2)_2]_3[V_{15}Sb_6O_{42}(H_2O)]\}\cdot8H_2O$ (**1**) crystallizes in the monoclinic space group *C*2/*c* (see Table 1) with three unique Sb atoms on general positions. One of the eight unique V atoms as well as one of the two Fe centers are located on special positions.

During structure refinement, two cluster anions with composition $[V_{15}Sb_6O_{42}(H_2O)]^{6-}$ with a ratio of 9:1 for the two orientations have been identified (see Figure 1). As expected, the anion is composed of a spherical shell of condensed VO_5 square pyramids, with the terminal V═O bonds directed out of the shell. The terminal V═O bond lengths around 1.6 Å are significantly shorter than the bridging V−μ_3-O bonds (≈1.9−2.1 Å; Table S1 in the Supporting Information), which is typical for VO_5 square pyramids.[13−15] In the center of the cluster, a water molecule is encapsulated. The central cluster motif can also be described as composed of two condensed V_6 hexagons approximately in a chair conformation, which are joined by three VO_5 pyramids and three Sb_2O_5 units, resulting in a V_6−V_3−V_6 stack as is the case in the molecular magnet $[V_{15}As_6O_{42}(H_2O)]^{6-}$ mentioned in the Introduction. The V−V separations fall within 2.876(2) and 3.054(2) Å, i.e., in the range reported for other antimonato polyoxovanadates. Bond-valence-sum (BVS) calculations[16] yield values for all V atoms close to 4.0 (4.02−4.13). Note that this result is supported by the frequency of the V═O symmetric stretching mode observed in the IR spectrum (see below). The BVS values for the two Fe^{2+} ions are 2.31 and 2.35 and those for Sb atoms between 3.13 and 3.27. The result of the BVS calculation justifies the notation $[V^{IV}{}_{15}Sb^{III}{}_6O_{42}(H_2O)]^{6-}$.

Table 1. Selected Technical Details of Data Collection and Results of the Structure Refinement of 1

cryst syst	monoclinic
space group	*C*2/*c*
a/Å	21.2896(14)
b/Å	21.0207(9)
c/Å	20.8609(13)
V/Å^3	9229.0
Z	4
$D_{calcd.}$/g cm^{-3}	2.277
μ/mm^{-1}	3.708
scan range/deg	1.98−25.94
reflns collected	30144
indep reflns	8945
reflns with $I > 2\sigma(I)$	6731
GOF on F^2	1.027
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0520, wR2 = 0.1199
R indices (all data)	R1 = 0.0759, wR2 = 0.1298
residual electron density/e Å^{-3}	1.337/−1.493

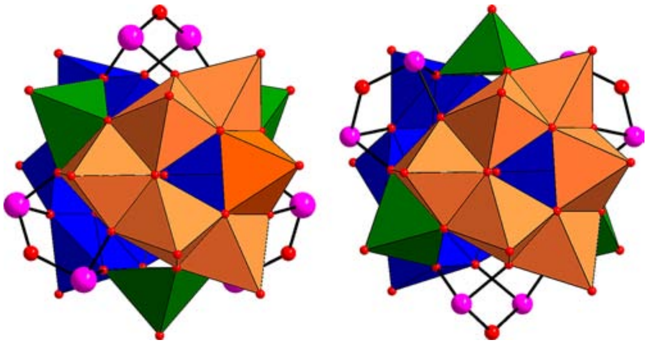

Figure 1. Two orientations of the $[V_{15}Sb_6O_{42}(H_2O)]^{6-}$ clusters: (left) majority cluster; (right) minority cluster.

The Sb_2O_5 units are formed by two trigonal-pyramidal corner-sharing SbO_3 groups yielding an arched, handle-like moiety with Sb−O bond lengths and O−Sb−O angles in good agreement with data reported for other antimonato polyoxovanadate cluster anions (Table S1 in the Supporting Information).[13−15] As mentioned before, BVS values for all Sb atoms are close to 3.0.

The cluster anion is expanded by $[Fe(C_6H_{14}N_2)_2]^{2+}$ complexes via Fe−O bonds [Fe−O = 2.105(5)−2.126(5) Å] to terminal O atoms of the cluster anion linking the $[V_{15}Sb_6O_{42}(H_2O)]^{6-}$ cores to form a three-dimensional network. Each $[Fe(C_6H_{14}N_2)_2]^{2+}$ is joined to two cluster anions; i.e., every $[V_{15}Sb_6O_{42}(H_2O)]^{6-}$ anion coordinates to six complex cations (see Figure 2). In the slightly distorted

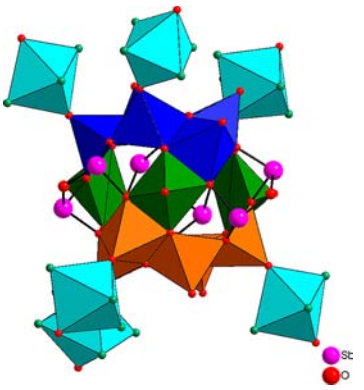

Figure 2. Structure of the $[V_{15}Sb_6O_{42}(H_2O)]$ cluster with the Fe^{2+}-centered complexes bound via Fe–O bonds. The VO_5 polyhedra of the V_6 hexagons are shown in two different colors. The three central VO_5 pyramids are displayed in green (Sb, purple; O, red; N, green).

octahedral Fe^{2+}-centered complexes, the Fe–N bonds span a narrow range from 2.171(7) to 2.222(7) Å. The Fe–N bond lengths and the N–Fe–N angles are comparable with values reported in the literature.[17–19]

The connection mode in **1** was never observed before in heterometal-expanded antimonato polyoxovanadates. We note that in $[(Co(en)_2)_2V_{14}Sb_8O_{42}(H_2O)]\cdot 6H_2O$[13a] the central $[V_{14}Sb_8O_{42}(H_2O)]$ core is bound to four Co^{2+} cations via terminal O atoms, leading to the formation of layers. Three-dimensional networks were realized in the compounds $[M_3V_{18}O_{42}(H_2O)_{12}(XO_4)]\cdot 24H_2O$ (M = Fe, Co; X = V, S), where terminal O atoms of the $\{V_{18}O_{42}\}$ cluster bind to six Fe^{2+}- and Co^{2+}-centered complexes, respectively, to form a highly symmetric structure with channels hosting the water molecules.[21] Recently, three-dimensional networks were also reported for germanato polyoxovanadates, e.g., for $\{[Cd_3(\mu\text{-dien})_2(Hdien)_2(H_2O)_2]Ge_4V_{16}O_{42}(OH)_4(H_2O)\}\cdot 2H_2O$ and for $[Co(pdn)_2]_3[Co_2(pdn)_4][V_{16}Ge_4O_{44}(OH)_2(H_2O)]\cdot 5H_2O$[22] and $[Co_2(en)_3][Co(en)_2]_2[Co(en)_2(H_2O)][V_{16}Ge_4O_{44}(OH)_2(H_2O)]\cdot 10.5H_2O$ (pdn = 1,2-propanediamine; en = ethylenediamine),[23] although their network topologies differ from that observed for the title compound. Analysis of the network topology using the program *TOPOS*[24] yields a sphere packing net 8/3/t1 with the Schläfli symbol $3^6\cdot 4^{16}\cdot 5^6$.

The three-dimensional network in **1** contains channels running along [001] measuring about 8.5 Å × 8.5 Å (Figure 3), with the Sb_2O_5 groups oriented toward the interior of the channel. These pores are occupied by crystal water, and the carbon skeleton of the amine ligands is also directed into the empty space of the pores. A second type of channel is running along [−110] with dimensions of ca. 8.5 Å × 11.9 Å for the elliptical cross section. Here the channel is occupied by a H_2O tetramer and parts of the organic ligands point into voids. As expected, the free space accessible for solvent molecules is small and amounts to only about 164 Å^3, which amounts to only 1.8% of the unit cell volume.[20]

Between the cluster anion and amine ligands as well as the water and amine ligands, strong N–H···O bonds are observed in the range of 2.1239(1)–2.6984(2) Å.

IR Spectroscopy. The IR spectrum shows the characteristic terminal $\nu(V{=}O_{term})$ vibration at 976 cm^{-1}, and the ν(V–O–V) absorption is located at 738 cm^{-1}. The assignment of the vibration modes is in accordance with the data published in the literature.[13–15] The IR spectrum also includes characteristic vibrations of the organic ligands and water: ν(OH) 3411 (s), ν(N–H) 3221 (s), ν(N–H) 1596 (s), $\nu(C{-}H_3)$ 2879, $\nu(C{-}H_2)$ 2820 (m) cm^{-1}.

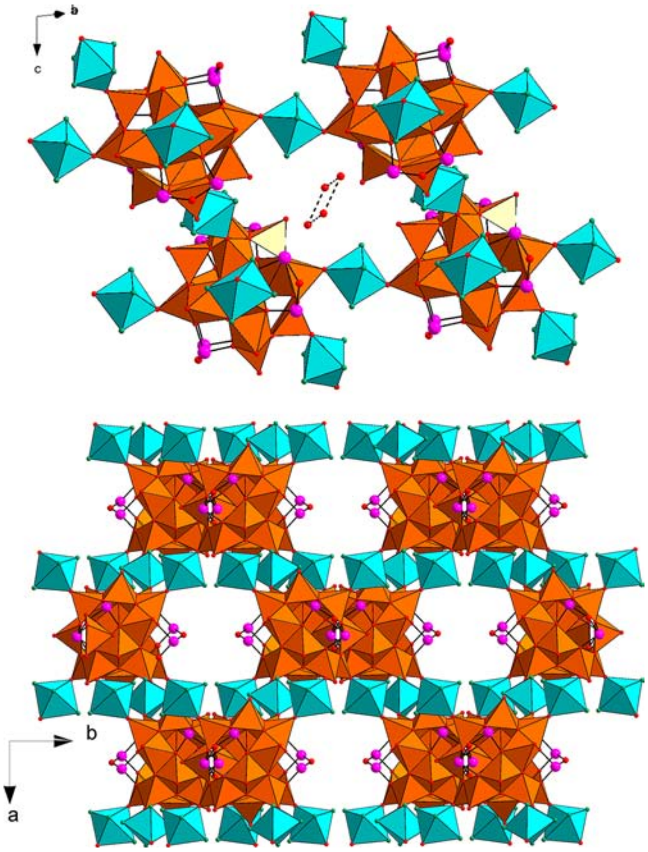

Figure 3. Three-dimensional network of $\{[Fe(C_6H_{14}N_2)_2]_3[V_{15}Sb_6O_{42}(H_2O)]\}$ in views emphasizing the channels along [001] (top) and [−110] (bottom). The H_2O tetramer is shown with dashed connectors. Organic groups and other water molecules are omitted for clarity.

UV–Vis Spectroscopy. The optical band gap was determined by applying the Kubelka–Munk method (Figure 4). According to this method, compound **1** with a value of 2.47 eV is a wide-gap semiconductor. In addition to the optical band

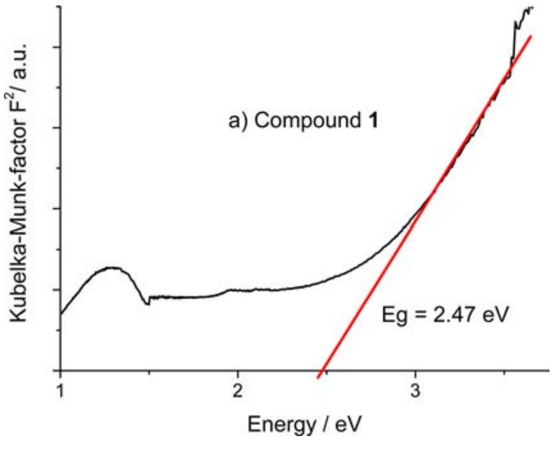

Figure 4. Determination of the optical band gap of compounds **1** and **2** from a UV–vis diffuse-reflectance spectrum using the Kubelka–Munk method.

gap, the absorption at 1.25 eV for **1** can be assigned to a d−d transition of Fe^{2+} ($^5T_2 \rightarrow {}^5E$).[25]

Magnetochemical Analysis. The low-field magnetic susceptibility of **1** (Figure 5) indicates ferromagnetic coupling between the $\{V_{15}Sb_6\}$ core cluster and the adjoined iron(II) diaminocyclohexane complexes linked to the terminal O sites of the vanadyl groups, which define the two outer V_6 hexagons of the $\{V_{15}Sb_6\}$ cluster. While the complexity of this spin cluster network prevents an analytical analysis of the magnetic data, a comparison of the experimental $\chi_m T$ data with the sum of the contributions of three Fe^{II} centers (per formula unit) and the data established for $\{V_{15}E_6\}$-type clusters (E = As, Sb) shows that the susceptibility data can be described by a simple mode, in which the data are decomposed into contributions from the $\{V_{15}Sb_6\}$ cluster, the individual Fe^{II} (s = 2) centers with their respective single-ion effects (for the ligand-field effects, the FeO_2N_4 coordination environments are assumed to be regular octahedral), and the consequences of coupling interactions that are accounted for by a simple Curie−Weiss-type term. Using the computational framework *CONDON 2.0*, least-squares fitting yields an Fe^{II} ligand-field parameter of $B_0^4 = 34000\ cm^{-1}$ (Wyborne notation) and an isotropic g value of 2.38, and a positive Weiss temperature θ = 1.91 K reflects the dominant ferromagnetic interactions between the Fe^{II} spin centers and between the Fe^{II} centers and vanadyl groups in the $\{V_{15}Sb_6\}$ clusters.

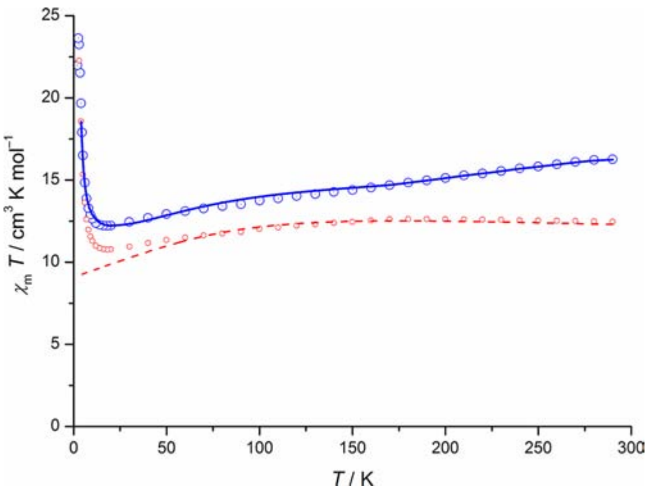

Figure 5. Temperature dependence of $\chi_{mol}T$ of **1** at an external static field of 0.1 T (experimental data: blue circles). Red circles: Experimental data with contribution from the $\{V_{15}Sb_6\}$ cluster are subtracted. Red dashed graph: Single-ion contributions from three noncoupled octahedrally coordinated Fe^{II} centers. Blue graph: Least-squares fit for the complete model including phenomenological Curie−Weiss-type coupling interactions. Note that only the temperature range 5−290 K was fitted, taking into account the simplifications of the model.

SUMMARY

The first antimonato polyoxovanadate compound exhibiting a three-dimensional network structure realized by the interconnection of $[V_{15}Sb_6O_{42}(H_2O)]$ cluster shells by Fe^{2+}-centered complexes was obtained under solvothermal conditions. The $[Fe(C_6H_{14}N_2)_2]^{2+}$ complexes are generated in situ during the reaction. Two different enantiomers of the cluster anion are observed. The network topology of $\{[Fe(C_6H_{14}N_2)_2]_3[V_{15}Sb_6O_{42}(H_2O)]\}$ is strikingly different from that observed for the $[M_3V_{18}O_{42}(H_2O)_{12}(XO_4)]\cdot 24H_2O$ (M = Fe, Co; X = V, S) compounds and the recently published three-dimensional germanato polyoxovanadates. The results of the magnetic investigations indicate that the spins on the Fe^{2+} ions interact with spins of the cluster anions, leading to dominating ferromagnetic exchange interactions at low temperatures. This observation is in contrast to other transition-metal cation-expanded antimonato polyoxovanadates where the magnetic moments of the two constituents barely interact with each other.

EXPERIMENTAL DETAILS

Compound **1** was prepared under solvothermal conditions in 15 mL glass tubes with Duran PBT screw caps. A mixture of $FeSO_4\cdot 7H_2O$ (150 mg, 0.54 mmol), NH_4VO_3 (150 mg, 1.21 mmol), Sb_2O_3 (250 mg, 0.84 mmol), *trans*-1,2-diaminocyclohexane (1 mL), and H_2O (3 mL) was heated at 160 °C for 7 days. After this time, the tube was allowed to cool to room temperature. The reaction product was collected by filtration and washed with water and ethanol. Compound **1** was obtained as dark-red needles, with a yield of 23% based on vanadium. Elem anal. Calcd for **1**: C, 13.93; H, 2.86; N, 5.42. Found: C, 14.05; H, 2.9; N, 5.51.

Crystal Structure Determination. The X-ray intensity data of single crystals of compound **1** were collected at 170 K using a STOE-1 Imaging Plate Diffraction System (IPDS-1) with Mo Kα radiation (λ = 0.71073 Å). The raw intensities were corrected for absorption. The structures were solved with *SHELXS-97*.[26] Crystal structure refinements were done against F^2 using *SHELXL-97*.[26] The non-H atoms except some of the disordered atoms of lower occupancy were refined using anisotropic displacement parameters. The C−H and N−H atoms were positioned with idealized geometry and were refined using a riding model. The H atoms of the water molecules could not be located but were considered in the calculation of the molecular weight. Some of the amine molecules are disordered and were refined using a split model. After structure refinement, residual electron densities were observed around the Sb_2O_5 dumbbells and near two VO_5 pyramids, which could be assigned to Sb and V atoms of a second cluster anion. Refinement of the site occupation factor yields a ratio of 9:1 and a reasonable structure model with Sb−O and V−O distances comparable to those retrieved from the literature.[13−16]

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 916468. Copies of the data can be obtained, free of charge, upon application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, U.K. [fax +44(0)1223−336033 or email deposit@ccdc.cam.ac.uk].

Solid-State UV−Vis Spectroscopy. UV−vis spectroscopy investigations were conducted at room temperature using a UV−vis two-channel Cary 5 spectrometer from Varian Techtron Pty., Darmstadt, Germany, equipped with an Ulbricht diffuse reflection accessory. The optical properties of the compounds were investigated by studying the UV−vis diffuce-reflectance spectrum of the powder sample. $BaSO_4$ was used as a reference material.

Elemental Analysis. CHN analyses were done using a EURO EA elemental analyzer, fabricated by EURO VECTOR Instruments and Software.

Magnetic Measurement. Magnetic susceptibility data of **1** were measured as a function of the field (0.1−5.0 T) and temperature (2.0−290 K) using a Quantum Design MPMS-5XL SQUID magnetometer. For simulations using *CONDON 2.0*,[27] the following standard Racah and spin−orbit constants have been employed for Fe^{II}: $B = 1058\ cm^{-1}$, $C = 3901\ cm^{-1}$, and $\zeta = 410\ cm^{-1}$.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Geometric parameters for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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