Polyoxometalates

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Organic Functionalization of Polyoxovanadates: Sb–N Bonds and Charge Control

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Numerous approaches towards the utilization of polyoxometalates (POMs) require their direct covalent attachment to organic groups. This ranges from immobilization of POM catalysts on polymer matrices and integration of POMs into porous metal–organic frameworks (MOFs) to electrochromic hybrid systems.[1] The synthesis strategies developed to date are predominantly not based on the formation of metal–organic bonds, but utilize other main-group elements as bonding mediators to link the organic functions to the POMs. These coupling reactions formally correspond to condensation of the POM cluster with alcohols or carboxylates (M–O–R),[2] or amines (M=N–R),[3] but also with organodiazenido, organophosphato, organosilyl, or organotin groups.[4] However, these strategies primarily target polyoxomolybdates and -tungstates. Various types of subsequent reactions of the organic functions attached to the POM (for example, 1,3-dipolar cycloadditions (“click” chemistry), Sonogashira and Heck coupling reactions, or Diels–Alder reactions)[5] emphasize the potential for the integration of such hybrid systems as building blocks into other structures. Polyoxovanadates, such as decavanadate, also exhibit interesting reactivities towards biomolecules, as exemplified by hydrolytic DNA cleavage,[6a] inhibition of oxygen consumption in membranes,[6b] or the inhibition of 6-phosphogluconate hydrogenase by tetravanadate.[6c]

Organopolyoxovanadates, however, are relatively rare. Their synthesis usually is limited to a formal exchange of terminal oxido sites with alkoxides or phosphonates, the integration of which strongly affects, or directs, the resulting structure of the vanadate framework.[7] Herein we present two examples that demonstrate how organic amines or ammonium groups can be added to existing polyoxovanadates through the formation of Sb–N bonds, whereby the framework structure is retained and the negative charge on it can be largely or completely compensated, which can increase the solubility the polyoxovanadates in organic solvents. Our approach is based on the recently discovered class of antimonate polyoxovanadates, such as the spherical cluster anions $[V_{16}Sb_4O_{42}(H_2O)]^{8-}$, $[V_{15}Sb_6O_{42}(H_2O)]^{6-}$, and $[V_{14}Sb_8O_{42}(H_2O)]^{4-}$.[8–10] Following systematic adjustments to the synthesis, which is strongly dependent on the pH value, we were able to isolate the organically functionalized analogues $[V^{IV}{}_{14}Sb^{III}{}_8(C_6H_{15}N_3)_4O_{42}(H_2O)]\cdot 4\,H_2O$ (**1**) and $(C_6H_{17}N_3)_2[V^{IV}{}_{15}Sb^{III}{}_6\ (C_6H_{15}N_3)_2O_{42}(H_2O)]\cdot 2.5\,H_2O$ (**2**), in which protonated amines bind to the spherical polyoxovanadate clusters through Sb–N bonds.

The structure of the two clusters in **1** and **2** can formally be derived from the archetypal spherical isopolyoxovanadate(IV) $\{V_{18}O_{42}\}$[11] by replacing four (in **1**) or three (in **2**) $O_4V{=}O$ square-based pyramids with an equal number of O_2Sb-(μ-O)SbO_2 groups (**1**: Sb-μ-O: 1.930(6)–2.031(5) Å, **2**: Sb-μ-O: 1.930(5)–2.040(4) Å). Abstraction of four VO_5 pyramids in $[V_{18}O_{42}]^{12-}$ results in the formation of two perpendicular, intersecting $(O_4V{=}O)_8$ rings of edge-sharing VO_5 pyramids (Figure 1 a). Both the geometric parameters of the Sb_2O_5 groups in **1** and **2** as well as the V-μ-O (1.912(6)–1.981(6) Å) and V-$O_{terminal}$ (1.584(7)–1.637(6) Å) bond lengths and V···V distances (2.818(2)–3.1011(19) Å) are in line with other antimony polyoxovanadates.[8–10]

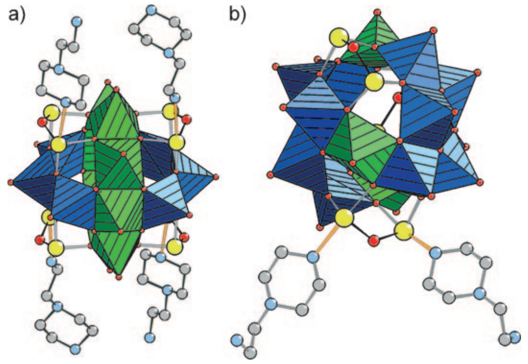

Figure 1. a) Polyhedral representation of the central $[V^{IV}{}_{14}Sb^{III}{}_8O_{42}(H_2O)]$ fragments of two eight-membered vanadyl rings (blue/green) in **1** with four Sb_2O_5 groups, to each of which a $C_6H_{15}N_3$ group is attached by a Sb–N bond (orange). b) The cluster anion $[V^{IV}{}_{15}Sb^{III}{}_6(C_6H_{15}N_3)_2O_{42}(H_2O)]^{4-}$ in **2**. The green $O{=}VO_4$ pyramids indicate the positions of the central V_3 triangle; O red, Sb yellow, N blue, C gray (H omitted).

The spherical $[V_{14}Sb_8O_{42}]^{4-}$ cluster in **1** encloses a water molecule in its central cavity. Of interest in **1** are the four Sb–N bonds to protonated 1-(2-aminoethyl)piperazine groups, which complete the charge-neutral $[V_{14}Sb_8(C_6H_{15}N_3)_4O_{42}(H_2O)]$ molecules. One of the two crystallographically independent 1-(2-aminoethyl)piperazinium cations binds to an Sb center through a terminal NH_2 group, the other binds to a different Sb site through the N atom of the piperazinium

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moiety (Sb—N: 2.528(7) and 2.536(9) Å). Bond valence sums (BVS) of the Sb atoms involved in the Sb—N bonds are 3.41 (Sb2) and 3.49 (Sb3), slightly exceeding those of the two remaining Sb centers (3.36 and 3.38). A search of the Cambridge structural database (CSD) for Sb—N bonds, focusing on SbO_3N units, yields short bond lengths to anionic species, such as NCS^-, and bonds around 2.45 Å to neutral N ligands,[12–15] Sb—N bonds involving cationic amines are unknown to date.

In the solid-state structure of **1** the clusters of approximately 11 Å in diameter are arranged in hexagonal layers in the (001) plane (Figure 2a); the polyoxovanadate cores and the organic ligands alternate along [001]. Clusters of neighboring layers are separated by about 3 Å. Exposed O sites are involved in several intra- and intermolecular contacts to hydrogen atoms of the N-H groups. The shortest O···H distance of 1.92 Å indicates a relatively strong hydrogen bond. Weak Sb–O interactions (ca. 2.73 Å) are evident between neighboring cluster units, these interactions organize the clusters into chains along *a*. In comparison, the clusters in $[(C_2N_2H_{10})_2\text{-}\beta\text{-}\{Sb_8V_{14}O_{42}(H_2O)\}](C_2N_2H_8)\cdot 4H_2O$ form weak Sb–O contacts (Sb–O: 2.79 and 2.74 Å), resulting in a double-chain arrangement.[15] The BVS value averaged over all the vanadium centers of nearly 4.0 confirms the formal oxidation state V^{IV}.

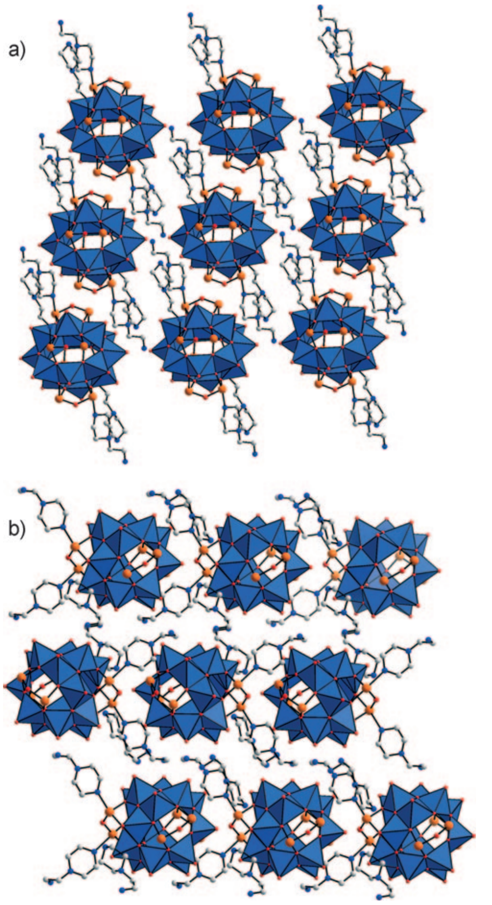

Figure 2. a) Arrangement of the cluster units in **1** within the (001) plane. b) Cluster arrangement within (001) in **2**. H_2O molecules, organic ammonium cations, and H atoms are omitted.

Compound **2** comprises the cluster anion $[V^{IV}_{15}Sb^{III}_6O_{42}(H_2O)]^{6-}$ (Figure 1b) to which two $C_6H_{15}N_3$ units are directly attached. Two doubly protonated amines per formula unit are situated between neighboring clusters as counterions. The structure of $[V_{15}Sb_6O_{42}(C_6H_{15}N_3)_2(H_2O)]^{4-}$ in **2** contains 15 VO_5 and 3 Sb_2O_5 groups. After formal removal of the VO_5 pyramids of the $\{V_{18}O_{42}\}$ archetype, three incomplete rings of seven edge-sharing VO_5 polyhedra remain that encapsulate a H_2O guest as in the case of **1**. The V-μ-O (1.900(5)–2.015(4) Å), V-$O_{terminal}$ (1.599(4)–1.632(5) Å), and Sb-O (1.930(5)–2.040(4) Å) bond lengths are comparable to those in **1**.

As observed for the arsenato-based analogue $[V_{15}As_6O_{42}(H_2O)]^{6-}$ with As_2O_5 groups,[14] the Sb_2O_5 groups, situated in the cluster's equatorial plane, induce a slight expansion of the cluster geometry compared to the isopolyoxovanadate $\{V_{18}O_{42}\}$ (cluster diameter in **2**: 11 Å). Two $C_6H_{15}N_3$ groups are bound to two of the six crystallographically independent Sb^{III} centers of the cluster through a piperazinium N atom (Sb1–N2: 2.542(6); Sb2–N12: 2.502(6) Å). BVS values of 3.44 and 3.48 for Sb1 and Sb2 are comparable to those of compound **1**. In the (100) plane, each $[V_{15}Sb_6O_{42}(C_6H_{15}N_3)_2(H_2O)]^{4-}$ cluster is surrounded by six nearest neighbors (Figure 2b). The clusters are arranged in rows along [100] and there is a uniform orientation of the amine groups. In contrast to **1**, the shortest intercluster Sb···O distances exceed 3 Å, ruling out significant intermolecular interactions. A complex three-dimensional O···H-type hydrogen-bond network (O···H distances range from 1.98 to 2.1 Å) interlinks the cluster units in the crystal structure of **2**. Remaining protonated amines and crystal water molecules are placed between the cluster layers.

Thermogravimetric measurements (TGA/DTA) indicate a comparably high stability of the Sb—N bonds. For **1**, a three-step endothermal decomposition is found. After the loss of its H_2O molecules (mass loss: $\Delta m_{exp} = 3.1\,\%$, $\Delta m_{calcd} = 3.04\,\%$; $T_{onset} = 115\,°C$) two $C_2H_4NH_3$ fragments are cleaved off in a second step only at $T_p = 253\,°C$ ($\Delta m_{exp} = 3\,\%$, $\Delta m_{calcd} = 3.04\,\%$). Above 300 °C a continuous decrease in mass is observed that is not complete at 700 °C. For **2**, water molecules are lost between 30 and 260 °C ($\Delta m_{exp} = 2.35\,\%$; $\Delta m_{calcd} = 2.29\,\%$). A complex decomposition sequence with two steps at $T_{onset} = 303$ and 323 °C is observed above 260 °C, followed by a nearly continuous mass loss up to 700 °C.

Both compounds are soluble in ethanol and methanol. The UV/Vis spectra of the solutions exhibit a strong absorption band at approximately 230 nm and a weaker shoulder at 280 nm. Electrospray mass spectra of the solutions are extremely complicated, resulting in signals up to around *m*/*z* 887.

The magnetic properties of **1** and **2** display a strong antiferromagnetic coupling mediated by μ-O bridges between the $s = 1/2$ vanadyl groups (Figure 3) that is typical for polyoxovanadate(IV) systems. The exchange interactions in the $\{V_{14}Sb_8\}$ fragment in **1** are complex (see Supporting Information); for **1**, $\chi_{mol}T$ for 0.1 Tesla decreases continuously

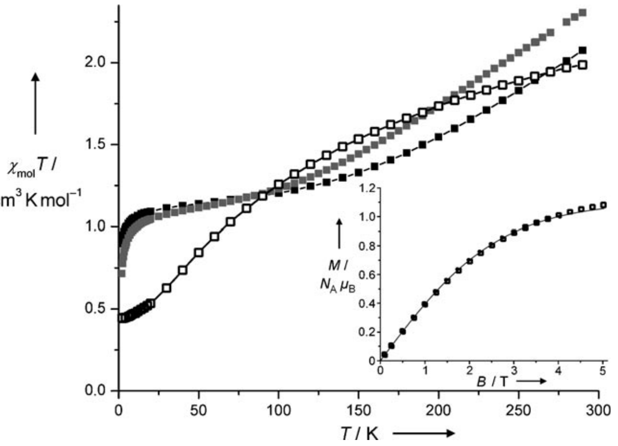

Figure 3. Temperature dependence of $\chi_{mol}T$ at $B_0 = 0.1$ Tesla (**1** open squares; **2** black; $(H_3tren)_2[V_{15}Sb_6O_{42}]\cdot 0.33\,tren\cdot 3\,H_2O$[9] gray; tren = tris(2-aminoethylamine). Inset: Field dependence of the magnetization of **2** at 2.0 K with a least-squares fit to a Brillouin function for $S = 1/2$.

with decreasing temperatures and below 6 K approaches 0.44 cm^3 K mol^{-1}, slightly larger than the value of 0.375 cm^3 K mol^{-1} ($g = 2.0$) expected for a possible $S = 1/2$ ground state. Field-dependent magnetization data recorded at 2.0 K corresponds to a Brillouin expression for $S = 1/2$ scaled to an unusually high $g = 2.17$. The temperature dependence of the susceptibility of **2** qualitatively matches that of $[V^{IV}_{15}As^{III}_6O_{42}(H_2O)]^{6-}$ and $[V^{IV}_{15}Sb^{III}_6O_{42}(H_2O)]^{6-}$. The $\{V_{15}E_6\}$ systems feature a central V_3 triangle in which weak antiferromagnetic superexchange ($J \approx -5$ K) is mediated by the O_2Sb-O-SbO_2 groups, whereas the vanadyl groups of the two outer V_6 rings are very strongly coupled and thus do not significantly contribute to the magnetization.[9,16] Compared to $\{V_{15}As_6\}$ and $\{V_{15}Sb_6\}$ systems, **2** displays weaker antiferromagnetic exchange in its V_3 fragment (corresponding to a weaker decrease below 30 K) and a slightly stronger exchange with the spin centers of the outer V_6 rings, as shown by a stronger increase at high temperature. These changes in the exchange energies underline that the frontier orbitals of the Sb_2O_5 groups are influenced by a significant covalent bonding component from the Sb–N bonds.

In conclusion, the formation of Sb–N bonds under hydrothermal conditions allows for a covalent expansion of antimonato polyoxovanadate architectures. Protonated organic amines can be attached to the polyanions in different binding modes, both through primary (**1**) and also through secondary (**1**, **2**) amines. The addition of these ammonium groups also results in a reduced total charge and, in turn, in a reduced solubility in the aqueous reaction solution, thus aiding subsequent precipitation of crystalline material.

Experimental Section

Both compounds were synthesized under hydrothermal conditions, where the pH value of the reaction solution plays a crucial role. The initial pH values of 12 (**1**) and 11.5 (**2**) decrease to 11.5 (**1**) and 10.5 (**2**) over the course of the reactions. An as yet unidentified green microcrystalline powder is formed for starting pH values < 11.

1: A mixture of NH_4VO_3 (600 mg, 5.12 mmol), Sb_2O_3 (600 mg 2.05 mmol), 1-(2-aminoethyl)piperazine (3 mL), and water (1 mL) in a 30 mL steel autoclave (PTFE lining) was heated to 180 °C for 7 days. After cooling the mixture to room temperature, brown-green crystals of **1** were collected by filtration, washed with acetone and water, and dried under air. Small quantities of Sb_2O_3 residues could be identified in the X-ray powder diffractogram. Yield: 24 % based on Sb. Typical crystal dimensions: $0.3 \times 0.1 \times 0.025$ mm^3. Elemental analysis (%): found: C 9.18, H 2.26, N 5.96; calcd: C 9.72, H 2.38, N 5.67.

2: NH_4VO_3 (800 mg, 6.84 mmol), Sb_2O_3 (400 mg, 1.37 mmol), 1-(2-aminoethyl)piperazine (2 mL), and water (2 mL) in a 30 mL steel autoclave (PTFE lining) were heated to 160 °C for 7 days. After cooling the mixture black crystals of **2** were collected by filtration, washed with distilled water and acetone, and dried under air. Typical crystal dimensions: $1.5 \times 0.5 \times 0.25$ mm^3. Yield: 64 % based on Sb. Elemental analysis (%): found: C 10.76, H 2.49, N 6.65; calcd: C 10.48, H 2.33, N 6.11.

Crystallographic data for **1**: $Z = 1$, $M_r = 2966.05$ g mol^{-1}, space group $P\bar{1}$, $a = 11.6308(7)$, $b = 13.0370(8)$, $c = 13.6252(9)$ Å, $\alpha = 101.128(7)°$, $\beta = 91.737(7)°$, $\gamma = 112.732(7)°$, $V = 1857.1(2)$ Å^3, $\rho_{calcd} = 6.383$ g cm^{-3}, $F(000) = 1404$, $\lambda = 0.71073$ Å, $T = 293$ K, $\mu = 4.621$ mm^{-1}, 10798 reflections, of which 5122 are unique, $R_{int} = 0.0675$. The structure was solved using direct methods and refined against F^2 ($\theta_{max} = 26.02°$), $R1(I > 2\sigma(I)) = 0.043$, $wR2 = 0.1037$, GoF = 0.963.

Crystallographic data for **2**: $Z = 1$, $M_r = 2750.496$ g mol^{-1}, space group $P\bar{1}$, $a = 12.0574(9)$, $b = 12.9922(9)$, $c = 25.5467(19)$ Å, $\alpha = 94.085(9)°$, $\beta = 101.042(9)°$, $\gamma = 111.651(8)°$, $V = 3606.3(5)$ Å^3, $\rho_{calcd} = 2.529$ g cm^{-3}, $F(000) = 2620$, $\lambda = 0.71073$ Å, $T = 293$ K, $\mu = 4.146$ mm^{-1}, 27887 reflections, of which 13928 are symmetry independent, $R_{int} = 0.0866$. The structure was solved using direct methods and refined against F^2 ($\theta_{max} = 25.99°$), $R1(I > 2\sigma(I)) = 0.0448$, $wR2 = 0.1129$, GoF = 0.999. CCDC 794602 (**1**) and CCDC 794603 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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