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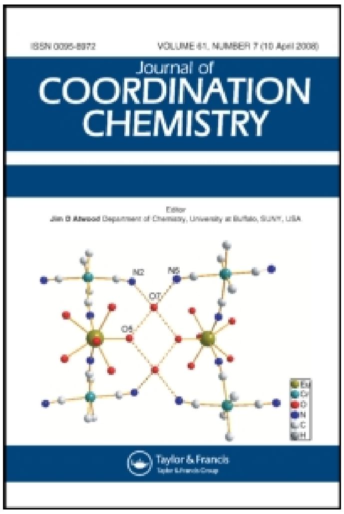

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Syntheses, structures, and magnetism of $\{V_{15}M_6O_{42}(OH)_6(Cl)\}$ (M = Si, Ge)

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Syntheses, structures, and magnetism of $\{V_{15}M_6O_{42}(OH)_6(Cl)\}$ (M = Si, Ge)

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Two $[V_{15}M_6(OH)_6O_{42}(Cl)]^{7-}$ (M = Si for **1**, Ge for **2**) cluster anions with protonated amines as counterions have been synthesized under hydrothermal conditions and characterized by FT-IR, energy dispersive spectroscopy, XPS, powder X-ray diffraction, thermogravimetric analysis (TGA), elemental analysis, and single-crystal X-ray analyses. Both compounds consist of $\{V_{15}M_6O_{42}(OH)_6(Cl)\}$ (M = Si for **1**, Ge for **2**), which are derived from $\{V_{18}O_{42}\}$ by substitution of three $\{VO_5\}$ square pyramids with three $\{Si_2O_5(OH)_2/Ge_2O_5(OH)_2\}$ units. It represents the first example of cage-like polyoxovanadates (POVs) containing three $(Si/Ge)_2O_5(OH)_2$ units. There are extensive hydrogen bonding interactions between POVs and organoamines in **1** and **2**. Compound **1** presents a close-packed layer aggregate, while **2** exhibits the packing of six-membered rings with a 1-D channel. Magnetism measurements demonstrate the presence of strong antiferromagnetic interaction between V^{IV} centers in **1**.

Keywords: Polyoxovanadates; Vanadosilicate; Vanadogermanate; Antiferromagnetic interaction

1. Introduction

Polyoxovanadates (POVs), which may contain fully oxidized, reduced, or mixed-valence vanadium centers containing from 3 to 34 vanadiums, have been widely investigated for their physicochemical properties and potential applications in catalysis, electrical conductivity, medicinal chemistry, and magnetism [1–5]. A subclass of reduced POVs, $\{V_{18}O_{42}\}$ contains only oxo-vanadium (IV) centers and consists of 18 edge and corner-shared $\{O{=}VO_4\}$ square pyramids [6–8] (scheme 1a). A number of group VA elements substitute giving vanadoarsenate and vanadoantimonate clusters from the $\{V_{18}O_{42}\}$ antitype have been studied [9–15]. However, only a few vanadosilicate and vandogermanate clusters have been reported [16–20]. Only two silicon-substituted POVs have been prepared: $Cs_{10.5}[(V_{16}O_{40})(Si_{4.5}V_{1.5}O_{10})] \cdot 3.5H_2O$ and $[H_4V_{18}O_{46}(SiO)_8(DAB)_4 \cdot (H_2O)] \cdot 4H_2O$ (DAB = 1,4-diaminobutane) [16, 17]. The structure types of vanadogermanate clusters, such as $(H_2DAB)_4[V_{14}O_{44}(GeOH)_8] \cdot 6H_2O$,

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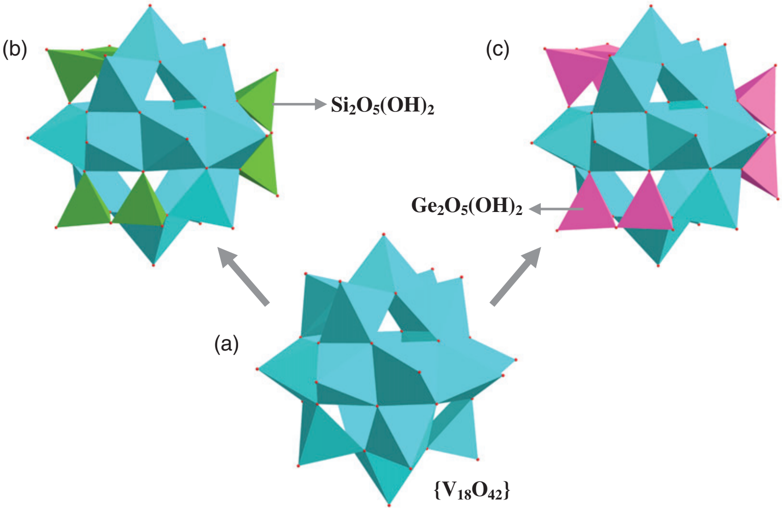

Scheme 1. The scheme of transformation of structures $\{V_{15}Si_6O_{42}(OH)_6\}$ and $\{V_{15}Ge_6O_{42}(OH)_6\}$ from the common type of $\{V_{18}O_{42}\}$. ($\{VO_5\}$ polyhedra: cyan).

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$Cs_8[Ge_4V_{16}O_{42}(OH)_4]\cdot 4.7H_2O$, $(pipH_2)_4(pipH)_4[Ge_8V_{14}O_{50}\cdot(H_2O)]$ (pip $= C_4N_2H_{10}$), and $(NH_4)_2[H_2V_9Ge_6O_{26}(L)_6]\cdot 0.65H_2O$ ($H_2L = HOCH_2CH_2OH$), were reported in 2003 by different research groups [17–19]. In 2006, Bensch *et al.* [20] reported two new mixed V–Ge compounds (dien-H_3)$_4[V_{14}Ge_8O_{42}S_8]\cdot 5H_2O$ (dien = diethylenetriamine) and (aep-H_3)$_4[V_{14}Ge_8O_{42}S_8]$ (aep = 1-(2-aminoethyl)piperazine).

In order to enrich examples of group IVA-substituted POVs, we incorporate silicon or germanium into the $\{V_{18}O_{42}\}$ system by adopting different organoamines as reducing agents, obtaining $(H_2pdn)_3(Hpdn)[V_{15}Si_6O_{42}(OH)_6(Cl)]\cdot nH_2O$ ($n = 7$–10; pdn = 1,3-propanediamine) (**1**) and $(H_2tren)_2(H_3tren)[V_{15}Ge_6O_{42}(OH)_6(Cl)]\cdot 2H_2O$ (tren = *tris*(2-aminoethyl)amine) (**2**). Both compounds consist of $\{V_{15}M_6O_{42}(OH)_6(Cl)\}$, derived from the $\{V_{18}O_{42}\}$ archetype by substitution of three $\{VO_5\}$ square pyramids with three $\{Si_2O_5(OH)_2/Ge_2O_5(OH)_2\}$ units (scheme 1b and c). No vanadosilicate and vanadogermanate cluster with $\{V_{15}M_6O_{42}\}$ (M = Si or Ge) structure types have been reported till now. The magnetic property further demonstrates the presence of strong antiferromagnetic interactions between V^{IV} centers in **1**.

2. Experimental

2.1. *Materials and methods*

All reagents and solvents were purchased from commercial sources and used without purification. The C, H, and N analyses were conducted on a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets from 4000–400 cm^{-1} on a Nicolet 170 SXFT/IR spectrometer. Energy dispersive spectroscopy (EDS) was performed on a JSM 5300 scanning electron microscope equipped with a PGT digital spectrometer. Powder X-ray diffraction (PXRD) samples were collected on a Japan Rigaku D/max γA X-ray diffractometer. The XPS spectra were recorded on an ESAY ESCA spectrometer with a Mg-Kα achromatic X-ray source. Thermogravimetric analysis (TGA) curves were performed on a 2960 SDT simultaneous thermal analyzer with a heating rate of 10°C min^{-1} under nitrogen. Variable temperature susceptibility measurements were carried out at 2–300 K on polycrystalline samples with a Quantum Design MPMS-5 magnetometer.

2.2. *Syntheses of 1 and 2*

2.2.1. Synthesis of $(H_2pdn)_3(Hpdn)[V_{15}Si_6O_{42}(OH)_6(Cl)]\cdot nH_2O$ ($n = 7$–10) (1). V_2O_5 (0.120 g, 0.66 mmol) was stirred in distilled water (5 mL) for 10 min. Then, pdn (1.10 mL, 13.2 mmol) and tetraethyl orthosilicate (TEOS; 0.50 mL, 2.25 mmol) were added with continuous stirring. The mixture was stirred for 60 min and the pH was adjusted to *ca* 9 with concentrated HCl. The resulting solution was sealed in a 15-mL Teflon-lined reactor, heated at 180°C for 6 days, and then cooled to room temperature. Brown block crystals of **1** (72.1% yield based on V_2O_5) were obtained by filtration, washed with distilled water, and dried in air. Anal. Calcd for $C_{12}H_{68}ClN_8O_{57.5}Si_6V_{15}$ (Calcd/Found (%) based on $7H_2O$) [15b]: C, 6.52; H, 3.10; N, 5.07. Found: C, 6.68; H, 3.13; N, 5.12. IR (KBr, cm^{-1}) ν: 3417 (w), 3121 (w), 1628 (m), 1501 (m), 1398 (m), 965 (m), 694 (s), 642 (s), 576 (s).

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2.2.2. Synthesis of $(H_2tren)_2(H_3tren)[V_{15}Ge_6O_{42}(OH)_6(Cl)]\cdot 2H_2O$ (2). NH_4VO_3 (0.07 g, 0.6 mmol) and GeO_2 (0.02 g, 0.2 mmol) were stirred in distilled water (5 mL) for 10 min. Then tren (0.2 mL, 1.30 mmol) was added with continuous stirring. The mixture was stirred for 60 min and the pH adjusted to 8–9 by concentrated HCl. The resulting solution was sealed in a 15-mL Teflon-lined reactor, kept at 170°C for 5 days, and finally cooled to room temperature. Brown block crystals of **2** (53.3% yield based on NH_4VO_3) were recovered by filtration, washed with distilled water, and dried in air. Anal. Calcd for $C_{18}H_{71}ClN_{12}O_{50}Ge_6V_{15}$ (%): C, 8.67; H, 2.87; N, 6.74. Found: C, 8.58; H, 2.92; N, 6.67. IR (KBr, cm^{-1}): 3471 (w), 3052 (w), 2898 (m), 1598 (m), 1479 (m), 1298 (m), 1074 (s), 976 (vs), 817 (s), 776 (s), 684 (s), 633 (s), 591 (s), 521 (s).

2.3. *X-ray crystallography*

Single-crystal X-ray diffraction data for **1** and **2** were conducted on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 296 K. All absorption corrections were applied using multi-scan. The structures were solved by direct methods (SHELXL-97) and refined through full-matrix least-squares on F^2 using SHELXL [21]. All hydrogens of the organoamines were placed in geometrically calculated positions and those of water molecules were not located. The detailed crystallographic data and structure refinement parameters of **1** and **2** are summarized in table 1.

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Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{12}H_{68}ClN_8O_{57.5}Si_6V_{15}$	$C_{18}H_{71}ClN_{12}O_{50}Ge_6V_{15}$
Formula weight	2212.83	2491.04
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$C2/c$
Unit cell dimensions (Å, °)		
a	14.9134(10)	12.8136(4)
b	22.3519(14)	23.7210(8)
c	21.0283(13)	23.2793(7)
α	90.00	90.00
β	95.0030(10)	98.7230(10)
γ	90.00	90.00
Volume (Å^3), Z	6982.9(8), 4	6993.9(4), 4
Calculated density (g cm^{-3})	2.054	2.346
$F(0\ 0\ 0)$	4260	4816
Reflections collected	93,234	24,157
Unique reflections	12,194	8602
Goodness-of-fit on F^2	1.053	1.000
R_{int}	0.0490	0.0208
Final R indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.0714$, $wR_2 = 0.2169$	$R_1 = 0.0490$, $wR_2 = 0.1493$
R indices (all data)	$R_1 = 0.0854$, $wR_2 = 0.2315$	$R_1 = 0.0554$, $wR_2 = 0.1565$

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^bwR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

3. Results and discussion

3.1. *Description of crystal structures*

Self-assembly of vanadium (V) source with TEOS/GeO_2 under hydrothermal conditions using organoamine reducing agents affords two reduced POVs. The pdn and tren reactants provide the sources not only of the counterbalance cations but also the reductant for V^{5+}. X-ray structural diffraction analysis reveals similar anionic clusters in both, $[V_{15}Si_6O_{42}(OH)_6(Cl)]^{7-}$ in **1** and $[V_{15}Ge_6O_{42}(OH)_6(Cl)]^{7-}$ in **2** (figure 1). The cluster anion with trigonal structure consists of 15 VO_5 square pyramids and six SiO_4 or GeO_4 tetrahedra. Two such tetrahedra are joined into a $(Si/Ge)_2O_5(OH)_2$ moiety. They can be related to the $\{V_{18}O_{42}\}$ structure by replacing three VO_5 square pyramids of $\{V_{18}O_{42}\}$ with three $(Si/Ge)_2O_5(OH)_2$ units. In the anion, the same coordination environments around all vanadiums are formed by a terminal and four μ_3-oxygens $\{(O{=})V(\mu_3\text{-}O)_4\}$, which have typical geometric parameters with V=O lengths of 1.595(5)–1.624(5) Å and V–O bond lengths of 1.904(5)–2.021(5) Å. The six Si/Ge atoms exhibit only one type coordination, one terminal, two μ_3- and one μ_2-oxygens $\{(O{=})(Si/Ge)(\mu_3\text{-}O)_2(\mu_2\text{-}O)\}$, which have bond distances ranging from 1.592(5) to 1.647(5) Å. V–V contacts range from 2.8809(17) to 3.0360(18) Å. Selected bond distances of both structures are listed in table S1.

Formation of the cluster units in two compounds is the same and we take **1** as example. Within the anionic clusters, the V–O square pyramids are divided into three groups: (1) three square pyramids (V3, V5, and V13) and three $Si_2O_5(OH)_2$ units are alternately held together to generate a triangular ring; (2) the other 12 square pyramids (V1, V10, V11, V12, V14, V15; V2, V4, V6, V7, V8, and V9) share their edges and vertexes to form two distorted hexagons on opposite sides of the triangular ring and connected with the ring by sharing 10 pairs of oxygens, giving rise to the spherical shell,

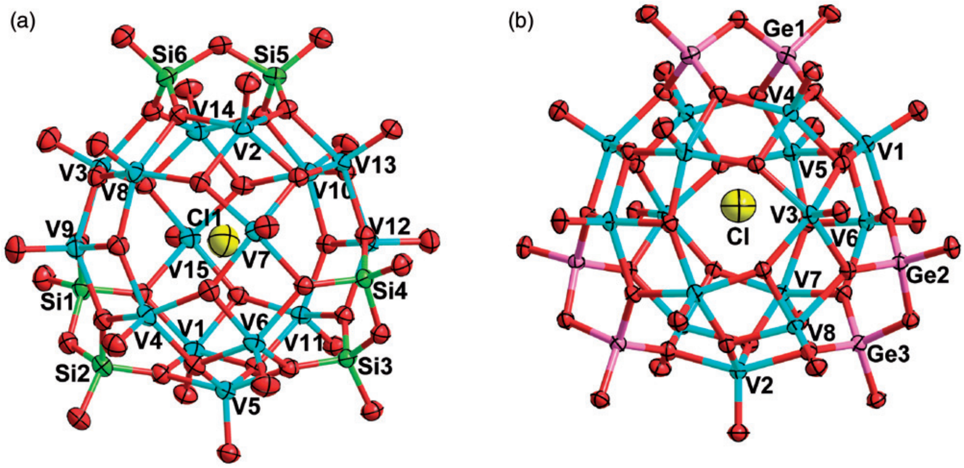

Figure 1. ORTEP drawings of (a) **1** and (b) **2** with thermal ellipsoids at 30% probability. All hydrogens and water molecules are omitted for clarity.

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$\{V_{15}Si_6O_{42}(OH)_6\}$ (figure 2). This represents the first example of cage-like POVs containing three $(Si/Ge)_2O_5(OH)_2$ units.

The negatively charged vanadium oxide shell in each compound hosts a chloride at its center, confirmed by EDS and XPS measurements. As shown in figure S1, though the average EDS analysis afford only a probable atom ratio of V/Si/Cl 15.79 : 6.32 : 1.05 and V/Ge/Cl 16.17 : 6.39 : 1.08, they strongly proved the presence of Cl^- in both structures. Moreover, the XPS measurements also display the peaks at 196.6 and 197.5 eV, ascribed to Cl_{2p} spin–orbit components (figure S2). There is no covalent interaction of chloride with the vanadium oxide framework, as shown by its average distance of 3.868 Å from the vanadium shell. Such inclusion of an anionic oxide cluster hosting an anionic guest into its hollow center has been reported in some clusters of POVs [3, 4].

As depicted in figure 3(a), there are extensive hydrogen bonds between terminal nitrogens of pdn cations and oxygens from $[V_{15}Si_6O_{42}(OH)_6(Cl)]^{7-}$ in **1**, in which the hydrogen bond distances are 2.6913–3.0638 Å. Each $[V_{15}Si_6O_{42}(OH)_6(Cl)]^{7-}$ is linked to 12 pdn cations and each pdn cation bridges three neighboring $[V_{15}Si_6O_{42}(OH)_6(Cl)]^{7-}$ anions *via* N–H $\cdots$ O hydrogen bonds. The N–H $\cdots$ O hydrogen bonds are responsible for the formation of the supramolecular architecture, which is similar to C–H $\cdots$ O hydrogen bonds in $[Fe(2,2'\text{-bipy})_3]_2[V^{V}_{7}V^{VI}_{9}O_{38}(Cl)] \cdot 4.67H_2O$ [22]. Compound **1** displays an {ABAB . . .} close-packed layer aggregate (figure 3b). (For the sake of clarity, we draw the packing schematic diagram of the polyanion clusters.)

Figure 4(a) shows the hydrogen bonding interactions between nitrogens of tren cations and oxygens of $[V_{15}Ge_6O_{42}(OH)_6(Cl)]^{7-}$ in **2**, with hydrogen-bonding distances from 2.6730 to 3.0497 Å. Each $[V_{15}Ge_6O_{42}(OH)_6(Cl)]^{7-}$ is connected with 20 tren cations and each tren cation links four neighboring $[V_{15}Ge_6O_{42}(OH)_6(Cl)]^{7-}$ anions *via* N–H $\cdots$ O hydrogen bonding interactions. N–H $\cdots$ O plays a key role in formation of the supramolecular network. Compound **2** exhibits the packing of six-membered rings in an {ABAB . . .} sequence with a 1-D channel (figure 4b).

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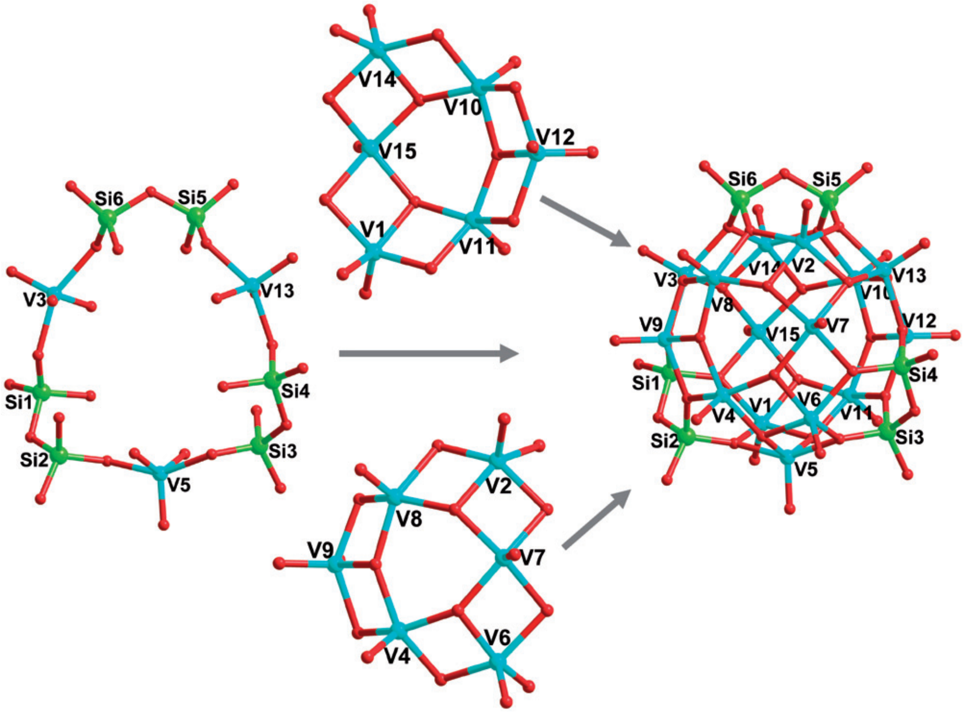

Figure 2. Ball-and-stick representations for the process of constructing the central cluster fragment [$V_{15}Si_6O_{42}(OH)_6$] in **1**.

3.2. *Bond valence sum and XPS spectra*

On the basis of bond valence sum (BVS) calculations [23], the average empirical oxidation states of V and Si are 4.110 and 3.975 in **1** and those of V and Ge are 4.120 and 4.042 in **2** (table S2), indicating that the oxidation state for each V, Si and Ge is +4. XPS measurements, for further confirmation of the oxidation states, give a peak at 515.7 eV ascribed to V^{4+} 2p and a peak at 101.9 eV attributed to Si^{4+} 2p in **1**. Comparably, in **2**, the energy regions of V 2p show one peak at 515.8 eV attributed to V^{4+} and a peak at 31.5 eV ascribed to Ge^{4+} (figure 5), consistent with the literature [24].

3.3. *FT-IR spectra and PXRD*

As shown in figure S3, IR spectra of **1** exhibit strong peaks at 965 cm^{-1} ascribed to $\nu(V{=}O)$ and four peaks at 965, 694, 642, and 576 cm^{-1} assigned to ν(M–O–M) and ν(Si–O) (M=V or Si) vibration modes. Peaks at 3417, 3121, 1628, 1501, and 1398 cm^{-1} are ascribed to characteristic vibrations of pdn. Compound **2** has characteristic bands at 817, 776, 684, 633, 591, and 521 cm^{-1} attributed to ν(M–O–M) and ν(M–O) (M=V or Ge), with strong bands at 976 cm^{-1} assigned to $\nu(V{=}O)$ bonds; characteristic absorptions of tren occur at 3052, 2898, 1598, 1479, and 1298 cm^{-1}.

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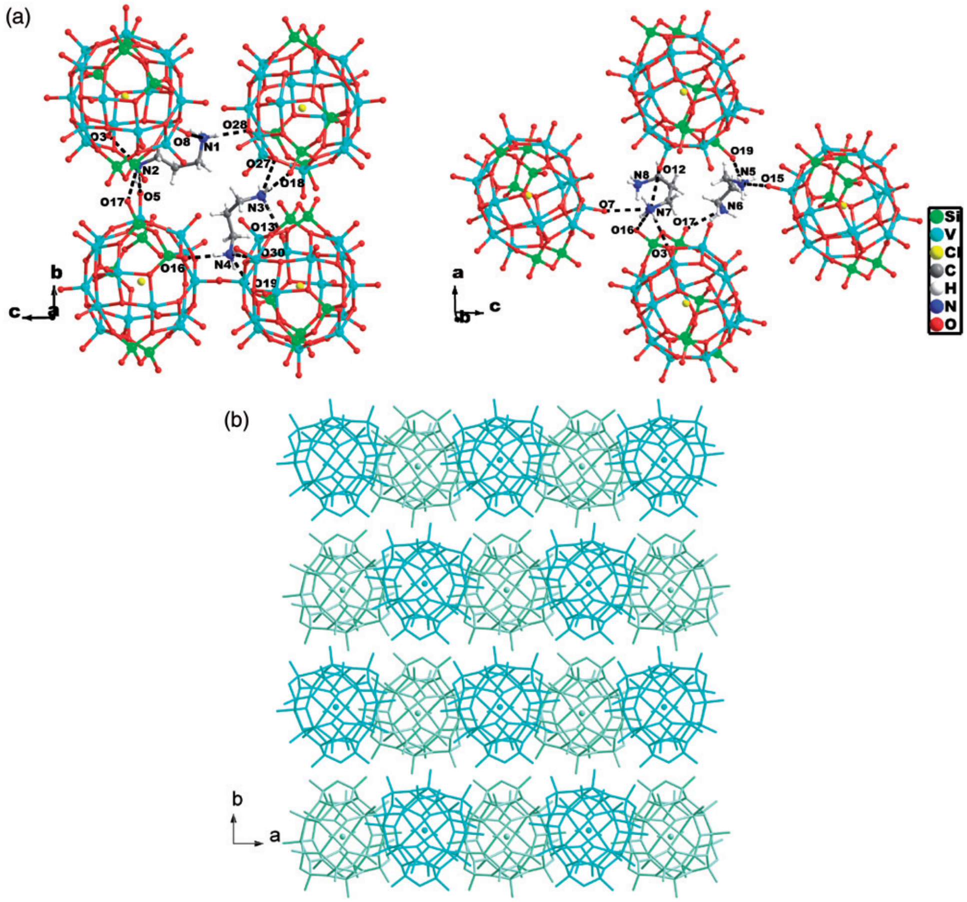

Figure 3. (a) View of the hydrogen bonds between pdn cations and adjacent $[V_{15}Si_6O_{42}(OH)_6(Cl)]^{7-}$ cluster anions. (b) Clusters of **1** display an {ABAB...} type of close-packed layers aggregate. The pdn cations and water are omitted for clarity.

PXRD patterns for both the compounds are presented in figure S4. Diffraction peaks of both experimental and simulated patterns match well in position, indicating their phase purity, ensuring the precision of other investigations.

3.4. *Thermogravimetric analyses*

TGA curve of **1** exhibits a first step weight loss of 5.83% to 115°C, assigned to seven water molecules in the structure. Compared with the crystal data, the different number of water molecules might be caused by dehydration in air. The second weight loss of 20.9% occurs from 115°C to 452°C, assigned to loss of four pdn ligands and Cl, in agreement with the calculated value (20.12%). Compound **2** shows a weight loss of 1.48% to 141°C, corresponding to release of two lattice water molecules (Calcd 1.45%). Then consecutive weight loss occurs from 141°C to 822°C with no obvious platform from loss of three tren ligands and Cl, but also with sublimation of GeO (figure S5).

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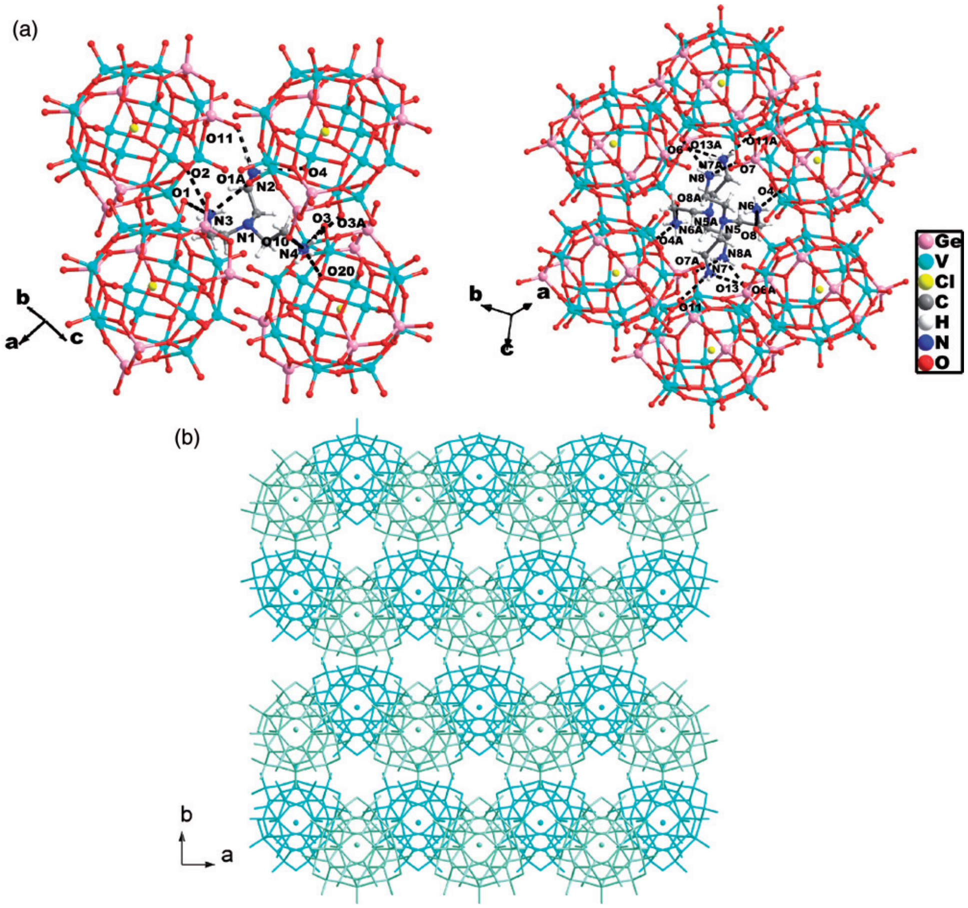

Figure 4. (a) View of the hydrogen bonds between tren cations and adjacent $[V_{15}Ge_6O_{42}(OH)_6(Cl)]^{7-}$ cluster anions. (b) Clusters of **2** exhibit six-membered rings with a 1-D channel. The tren cations and water are omitted for clarity.

3.5. *Magnetic property*

With same paramagnetic isostructural cluster, we can anticipate similar magnetic properties for them. We carried out variable temperature magnetic susceptibility on **1** from 2 to 300 K at 1000 Oe (figure 6). The cluster contains 15 V^{4+} ions with d^1 electronic configuration and exhibits a magnetic moment of *ca* 2.96 $cm^3\,K\,mol^{-1}$ at room temperature, much lower than the expected value (5.625 $cm^3\,K\,mol^{-1}$ for g=2.0) for the 15 unpaired electrons. When lowering the temperature, $\chi_M T$ shows a marked decrease and stabilizes at about 1.16 $cm^3\,K\,mol^{-1}$ at 35 K. Below 10 K, the magnetic moment decreases abruptly to 0.66 $cm^3\,K\,mol^{-1}$ at 2 K. The room temperature $\chi_M T$ value indicates the presence of seven or eight independent S=1/2 (V^{IV}, $3d^1$) centers. It is possible that both the V $\cdots$ V distance (<3.0659 Å) and the angle at the bridging oxygen play an important role for such strong antiferromagnetic interactions.

In summary, two compounds containing the first $[V_{15}M_6O_{42}(OH)_6(Cl)]^{7-}$ (M=Si, Ge) cluster anion with strong antiferromagnetic interaction between V^{IV} centers

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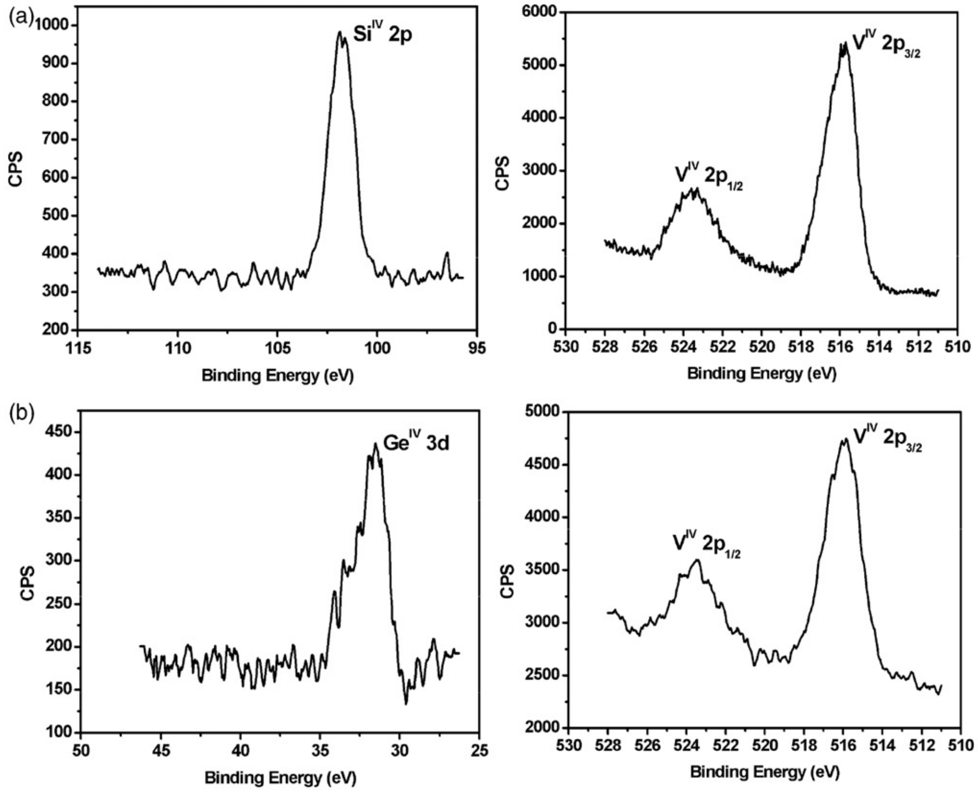

Figure 5. The XPS spectra for Si and V in (a) **1** and for Ge and V in (b) **2**.

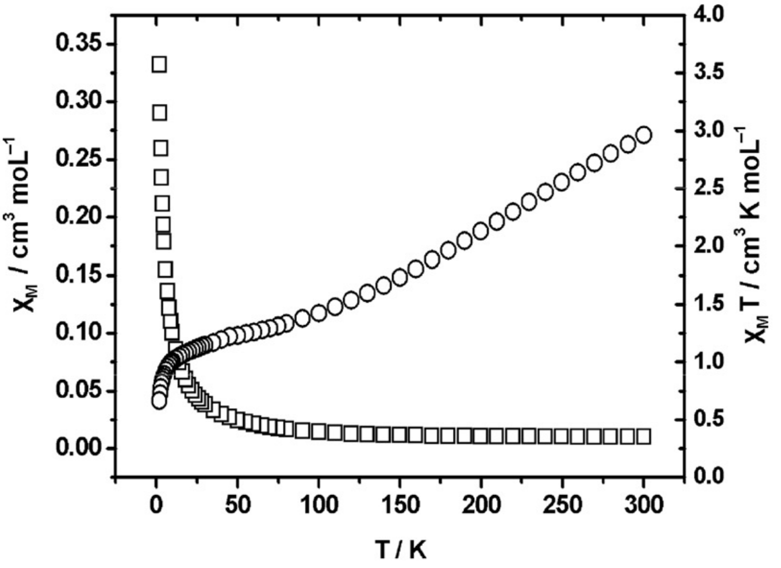

Figure 6. The temperature dependences χ_M (□) and $\chi_M T$ (○) for **1**.

have been prepared under hydrothermal conditions, representing the first cage-like POV clusters containing three $(Si/Ge)_2O_5(OH)_2$ units. There are extensive N–H $\cdots$ O hydrogen bonding interactions between POVs and organoamines in the two title complexes, in which N–H $\cdots$ O plays the key role in the formation of the supramolecular network. Their isolation significantly enriches the field of main group containing modified POVs and promotes the further development of POM chemistry. More detailed magnetic research and syntheses of a series of derivatives of **1** and **2** will be reported in the future.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center with the CCDC reference numbers 765788 and 765789 for **1** and **2**, respectively. 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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