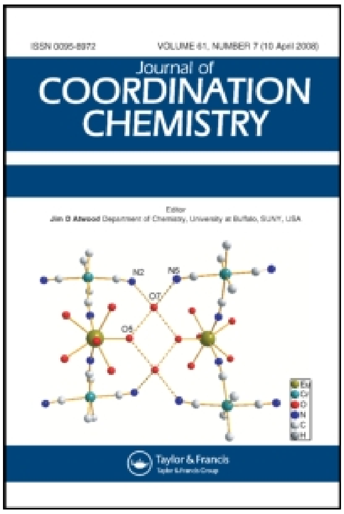

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Hydrothermal synthesis and characterization of two new arsenic-vanadate compounds with the same cluster anion $[As_8V_{14}O_{42}(H_2O)]^{4-}$

Guangpeng Zhou[a]; Chunyan Guo[a]; Wei Liu[a]; Yan Xu[a]; Xuefang Zheng[b]
[a] Institute of Chemistry for Functionalized Materials, College of Chemistry and Chemical Engineering, Liaoning Normal University, P.R., China [b] Liaoning Key Laboratory of Bio-Organic Chemistry, Dalian University, Dalian, P.R., China

To cite this Article Zhou, Guangpeng , Guo, Chunyan , Liu, Wei , Xu, Yan and Zheng, Xuefang(2008) 'Hydrothermal synthesis and characterization of two new arsenic-vanadate compounds with the same cluster anion $[As_8V_{14}O_{42}(H_2O)]^{4-}$', Journal of Coordination Chemistry, 61: 2, 202 — 210, First published on: 22 September 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958970701323996
URL: http://dx.doi.org/10.1080/00958970701323996

Journal of Coordination Chemistry
Vol. 61, No. 2, 20 January 2008, 202–210

Hydrothermal synthesis and characterization of two new arsenic–vanadate compounds with the same cluster anion $[As_8V_{14}O_{42}(H_2O)]^{4-}$

GUANGPENG ZHOU†, CHUNYAN GUO†, WEI LIU†,
YAN XU*† and XUEFANG ZHENG‡

†Institute of Chemistry for Functionalized Materials, College of Chemistry
and Chemical Engineering, Liaoning Normal University, No. 850,
Huanghe Road, Dalian 116029, P.R. China
‡Liaoning Key Laboratory of Bio-Organic Chemistry,
Dalian University, Dalian 116622, P.R. China

(*Received 9 August 2006; revised 19 October 2006; in final form 23 October 2006*)

Two new arsenic–vanadate compounds $[Co(C_4H_{13}N_3)_2]_2[As_8V_{14}O_{42}(H_2O)]\cdot 3.5H_2O$ (**1**) and $(C_2N_2H_9)_2(C_2N_2H_{10})[As_8V_{14}O_{42}(H_2O)]\cdot 2.33H_2O$ (**2**) have been hydrothermally synthesized and characterized by X-ray single crystal diffraction, IR spectra and thermogravimetric analysis. Compound **1** crystallizes in the monoclinic space group $P_2(1)/c$, $a = 24.649(9)$ Å, $b = 13.364(5)$ Å, $c = 22.463(8)$ Å, $\beta = 104.008(5)°$, $V = 7180(5)$ Å^3, $Z = 4$, $R_1 = 0.0787$, and $wR_2 = 0.1859$. Compound **2** crystallizes in rhombohedral system with space group $R3c$, $a = b = c = 22.2405(5)$ Å, $\alpha = \beta = \gamma = 110.4030(10)°$, $V = 8163.4(3)$ Å^3, $Z = 6$, $R_1 = 0.0341$ and $wR_2 = 0.0941$. The structural analyses show that both compounds have the same discrete cluster anion $[As_8V_{14}O_{42}(H_2O)]^{4-}$. Moreover, in **1**, the polyanions are connected through van der Waals forces to generate soft channels that are filled by $[Co(C_4H_{13}N_3)_2]^{2+}$ cations and water. In **2**, water and organic molecules link cluster anions to create the supramolecular assembly through hydrogen bonding.

Keywords: Arsenic–vanadate; Cluster; Hydrothermal synthesis; Crystal structure

1. Introduction

Efforts have been made to synthesize polyoxometalates due to their structural flexibility and potential functions as selective adsorption materials and heterogeneous catalysts [1–6]. An important family of polyoxometalates is arsenic–vanadium clusters. Many arsenic–vanadium clusters with different crystal structures have been reported [7–20]. In comparison to Mo–V–O [21–24] and W–V–O [25] clusters, they are still very limited because of the difficulties to prepare high quality single crystals for the structural analysis. Some As_8V_{14} clusters with different anions have been synthesized,

---

*Corresponding author. Email: yanxu@lnnu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701323996

such as $Rb_5[(As_2O)_4(VO)_2V_{12}O_{36}Cl] \cdot 2H_2O$ [26], $(enH_2)_{3.5}[As_8V_{14}O_{42}(PO_4)] \cdot 2H_2O$ [27], $[As_8V_{14}O_{42}(CO_3)][Cu(en)_2]_3 \cdot 10H_2O$ [28], and $[As_8V_{14}O_{42}(SO_4)]^{6-}$ [29, 30]. While most cluster centers were occupied by an anion, a few examples of $As_8V_{14}O_{42}$ cluster center-occupied by neutral molecules were reported [6, 31, 32]. Here we report two cluster compounds, as $[Co(C_4H_{13}N_3)_2]_2[As_8V_{14}O_{42}(H_2O)] \cdot 3.5H_2O$ (**1**) and $(C_2N_2H_9)_2(C_2N_2H_{10})[As_8V_{14}O_{42}(H_2O)] \cdot 2.33H_2O$ (**2**), which have the same cluster anion $[As_8V_{14}O_{42}(H_2O)]^{4-}$; Co^{2+} and protonated ethylenediamine cations serve as the charge-compensation components for **1** and **2**. Furthermore, water and organic molecules link cluster anions to create the supramolecular assembly through hydrogen bonds.

2. Experimental

2.1. *Materials and methods*

All chemicals are commercially available and were used without further purification. C, H, and N analyses were carried out on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Bruker Optik Gmbh spectrophotometer (range: 400–4000 cm^{-1}) as KBr pellets. Thermogravimetric (TG) analysis of both compounds were carried out under N_2 on a Diamond TG/DTA instrument (Perkin-Elmer) from 50 to 800°C and at a heating rate of 10°C min^{-1}.

Compound **1** was synthesized by the hydrothermal method. Typically, a mixture of V_2O_5 (0.18 g), Na_3AsO_4 (0.42 g), $CoCl_2 \cdot 6H_2O$ (0.24 g), $C_4H_{13}N_3$ (diethylenetriamine, 1.06 g) and H_2O (3.34 g) was stirred for ca 30 min in air and neutralized to $pH = 8.0$ with sulfuric acid (33%) before sealing in a 24 mL Teflon-lined autoclave at 170°C for seven days. Brown block crystals were obtained (0.12 g, yield 32.7% based on V) after being cooled to room temperature, filtration, washing with water, and air-drying. Analysis found: C, 7.42; N, 6.52; H, 2.39% (Calcd: C, 7.40; N, 6.47; H, 2.35%).

Similarly, a mixture of V_2O_5 (0.09 g), As_2O_3 (0.10 g), $CuCl_2 \cdot 2H_2O$ (0.04 g), $C_2N_2H_8$ (ethylenediamine, 1.42 g) and H_2O (1.07 g) was stirred for ca 30 min in air and neutralized to $pH = 6.0$ with hydrochloric acid (18%) before sealing in a 24 mL Teflon-lined autoclave at 170°C for seven days. Black block crystals were obtained (0.1 g, yield 63.5% based on V) after being cooled to room temperature, filtration, washing with water, and air-drying. Analysis found: C, 3.24; N, 3.84; H, 1.60% (Calcd: C, 3.23; N, 3.77; H, 1.56%).

Single crystals of **1** and **2** were chosen and placed onto a thin glass fiber by epoxy glue in air for data collection. Diffraction data were collected on a Bruker Apex2 CCD with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K using ω–2θ scan method. An empirical absorption correction was applied. Crystal data collection, parameters and refinement statistics for **1** and **2** are listed in table 1. Selected bond lengths are given in tables 2 and 3. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms of organic molecule for both compounds were refined in calculated positions, assigned isotropic thermal parameters, and allowed to ride on their parent atoms. All calculations were performed using the SHELX97 program package [33].

Table 1. Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{16}H_{61}As_8Co_2N_{12}O_{46.50}V_{14}$	$C_6H_{34.67}As_8N_6O_{45.33}V_{14}$
Formula weight	2596.15	2228.92
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Rhombohedral
Space group	$P2(1)/c$	$R3c$
a (Å)	24.649(9)	22.2405(5)
b (Å)	13.364(5)	22.2405(5)
c (Å)	22.463(8)	22.2405(5)
α (°)	90	110.4030(10)
β (°)	104.008(5)	110.4030(10)
γ (°)	90	110.4030(10)
Volume (Å^3)	7180(5)	8163.4(3)
Z	4	6
ρ (g cm^{-3})	2.402	2.720
μ (mm^{-1})	5.936	7.221
$F(000)$	5012	6368
Crystal size (mm^{-3})	$0.20 \times 0.18 \times 0.14$	$0.10 \times 0.10 \times 0.08$
θ range (°)	1.86–25.00	1.93–27.00
Limiting indices	$-29 \leq h \leq 28$, $-15 \leq k \leq 15$, $-16 \leq l \leq 26$	$-28 \leq h \leq 25$, $-28 \leq k \leq 27$, $-20 \leq l \leq 28$
Reflections collected/unique	33619/12304 [$R_{(int)} = 0.0680$]	48557/11580 [$R_{(int)} = 0.0345$]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and Min. transmission	0.4904 and 0.3831	0.5958 and 0.5321
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	12304/78/901	11580/84/716
Goodness-of-fit on F^2	1.144	1.055
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0787$, $wR_2 = 0.1859$	$R_1 = 0.0341$, $wR_2 = 0.0941$
R indices (all data)	$R_1 = 0.1169$, $wR_2 = 0.1971$	$R_1 = 0.0401$, $wR_2 = 0.0967$
Largest diff. peak and hole (e A^{-3})	1.758 and −1.365	1.918 and −0.873

3. Results and discussion

Structural analysis showed that both compounds have a discrete cluster anion $[As_8V_{14}O_{42}(H_2O)]^{4-}$. As previously reported, the polyanion is composed of one central water molecule, eight arsenic-oxygen trigonal pyramids (AsO_3) and fourteen vanadium–oxygen square pyramids (VO_5). As shown in figure 1, eight vanadium–oxygen square pyramids connect to each other by sharing edges, to form a central V_8 belt, in which all the vanadium atoms are approximately coplanar. Another six vanadium–oxygen square pyramids form two V_3O_7 fragments, which are bonded by bridging oxygen atoms above and below this V_8 belt. Moreover, the two V_3O_7 moieties together with the V_8 belt create a $V_{12}O_{38}$ shell. In addition, every two AsO_3 units connect to each other by bridging oxygen atoms to form a handle-like As_2O_5 moiety. The four As_2O_5 moieties join the $V_{12}O_{38}$ shell to make the polyanion $[As_8V_{14}O_{42}]^{4-}$, the center of which is occupied by a water molecule. In both compounds, the bond distances of V–O are 1.565(7)–1.624(3) Å for V–Ot and 1.886(5)–2.025(3) Å for V–Ob, while the As–O bond lengths vary from 1.741(6) to 1.795(5) Å, and the angles for O–V–O are between 76.3(2) and 150.1(2)°. These distances and angles are comparable to those found in similar structures.

Table 2. Selected bond lengths (Å) for compound **1**.

As(1)–O(16)	1.766(4)	V(3)–O(21)	1.919(5)	V(10)–O(8)	1.972(5)
As(1)–O(41)	1.768(5)	V(3)–O(15)	2.016(5)	V(10)–O(9)	1.994(5)
As(1)–O(4)	1.773(5)	V(3)–O(20)	2.020(5)	V(11)–O(29)	1.579(7)
As(2)–O(25)	1.753(5)	V(4)–O(37)	1.597(5)	V(11)–O(24)	1.963(5)
As(2)–O(40)	1.757(5)	V(4)–O(17)	1.913(5)	V(11)–O(23)	1.971(5)
As(2)–O(1)	1.780(6)	V(4)–O(14)	1.947(5)	V(11)–O(16)	1.979(5)
As(3)–O(28)	1.747(6)	V(4)–O(28)	1.977(5)	V(11)–O(7)	1.994(5)
As(3)–O(41)	1.770(5)	V(4)–O(3)	1.984(5)	V(12)–O(12)	1.597(6)
As(3)–O(24)	1.770(4)	V(5)–O(10)	1.603(5)	V(12)–O(2)	1.886(5)
As(4)–O(15)	1.763(5)	V(5)–O(5)	1.903(5)	V(12)–O(19)	1.932(5)
As(4)–O(40)	1.777(5)	V(5)–O(22)	1.918(5)	V(12)–O(16)	1.985(5)
As(4)–O(26)	1.795(5)	V(5)–O(9)	1.990(6)	V(12)–O(23)	2.004(5)
As(5)–O(7)	1.750(4)	V(5)–O(6)	1.999(6)	V(13)–O(18)	1.586(5)
As(5)–O(9)	1.771(6)	V(6)–O(30)	1.591(6)	V(13)–O(2)	1.935(5)
As(5)–O(35)	1.784(5)	V(6)–O(27)	1.920(5)	V(13)–O(19)	1.939(5)
As(6)–O(8)	1.765(6)	V(6)–O(22)	1.932(5)	V(13)–O(1)	1.965(5)
As(6)–O(35)	1.765(5)	V(6)–O(42)	2.010(5)	V(13)–O(26)	1.968(5)
As(6)–O(23)	1.770(5)	V(6)–O(25)	2.021(5)	V(14)–O(32)	1.610(5)
As(7)–O(3)	1.741(6)	V(7)–O(39)	1.595(6)	V(14)–O(5)	1.898(6)
As(7)–O(20)	1.746(5)	V(7)–O(5)	1.937(5)	V(14)–O(14)	1.928(5)
As(7)–O(36)	1.772(5)	V(7)–O(14)	1.940(6)	V(14)–O(6)	1.987(5)
As(8)–O(6)	1.753(6)	V(7)–O(24)	1.984(4)	V(14)–O(3)	1.992(5)
As(8)–O(42)	1.756(5)	V(7)–O(7)	2.005(5)	Co(1)–N(6)	2.134(8)
As(8)–O(36)	1.780(5)	V(8)–O(13)	1.598(5)	Co(1)–N(5)	2.154(7)
V(1)–O(31)	1.565(7)	V(8)–O(21)	1.926(5)	Co(1)–N(4)	2.154(7)
V(1)–O(15)	1.955(5)	V(8)–O(19)	1.929(5)	Co(1)–N(2)	2.176(8)
V(1)–O(20)	1.974(5)	V(8)–O(26)	1.966(5)	Co(1)–N(1)	2.192(7)
V(1)–O(25)	1.989(5)	V(8)–O(4)	1.995(5)	Co(1)–N(12)	2.207(9)
V(1)–O(42)	1.995(5)	V(9)–O(33)	1.605(5)	Co(2)–N(3)	2.155(9)
V(2)–O(11)	1.604(5)	V(9)–O(27)	1.916(5)	Co(2)–N(9)	2.179(9)
V(2)–O(21)	1.922(5)	V(9)–O(2)	1.939(5)	Co(2)–N(8)	2.194(10)
V(2)–O(17)	1.929(5)	V(9)–O(1)	1.960(5)	Co(2)–N(11)	2.196(9)
V(2)–O(28)	1.996(5)	V(9)–O(8)	1.976(5)	Co(2)–N(7)	2.207(9)
V(2)–O(4)	1.996(5)	V(10)–O(34)	1.606(5)	Co(2)–N(10)	2.212(9)
V(3)–O(38)	1.581(6)	V(10)–O(22)	1.915(5)		
V(3)–O(17)	1.915(5)	V(10)–O(27)	1.935(5)		

Table 3. Selected bond lengths (Å) for compound **2**.

As(1)–O(31)	1.771(3)	V(2)–O(31)	1.982(3)	V(9)–O(40)	1.604(3)
As(1)–O(20)	1.787(3)	V(2)–O(9)	1.987(3)	V(9)–O(5)	1.918(2)
As(1)–O(35)	1.794(3)	V(3)–O(4)	1.600(4)	V(9)–O(2)	1.942(3)
As(2)–O(9)	1.768(3)	V(3)–O(14)	1.930(2)	V(9)–O(24)	1.975(2)
As(2)–O(35)	1.771(2)	V(3)–O(29)	1.933(3)	V(9)–O(30)	1.986(3)
As(2)–O(24)	1.772(3)	V(3)–O(22)	1.992(3)	V(10)–O(33)	1.593(4)
As(3)–O(26)	1.779(3)	V(3)–O(12)	1.994(2)	V(10)–O(2)	1.934(3)
As(3)–O(10)	1.789(3)	V(4)–O(39)	1.624(3)	V(10)–O(29)	1.941(3)
As(3)–O(25)	1.791(3)	V(4)–O(2)	1.938(2)	V(10)–O(9)	1.996(2)
As(4)–O(23)	1.770(3)	V(4)–O(5)	1.944(3)	V(10)–O(17)	2.002(2)
As(4)–O(30)	1.773(3)	V(4)–O(13)	1.965(3)	V(11)–O(42)	1.590(3)
As(4)–O(25)	1.778(3)	V(4)–O(17)	1.969(3)	V(11)–O(10)	1.960(3)
As(5)–O(18)	1.761(3)	V(5)–O(32)	1.610(4)	V(11)–O(20)	1.968(3)
As(5)–O(22)	1.774(3)	V(5)–O(19)	1.919(2)	V(11)–O(30)	1.980(2)
As(5)–O(28)	1.778(3)	V(5)–O(16)	1.924(2)	V(11)–O(24)	1.988(3)
As(6)–O(17)	1.769(3)	V(5)–O(41)	1.990(3)	V(12)–O(6)	1.620(3)
As(6)–O(15)	1.777(3)	V(5)–O(26)	1.995(3)	V(12)–O(1)	1.926(3)
As(6)–O(12)	1.790(3)	V(6)–O(3)	1.608(3)	V(12)–O(16)	1.940(3)

(*Continued*)

Table 3. Continued.

As(7)–O(27)	1.771(3)	V(6)–O(16)	1.916(3)	V(12)–O(26)	1.962(2)
As(7)–O(15)	1.776(3)	V(6)–O(1)	1.919(3)	V(12)–O(23)	1.976(3)
As(7)–O(13)	1.796(3)	V(6)–O(27)	1.983(3)	V(13)–O(37)	1.593(3)
As(8)–O(41)	1.782(3)	V(6)–O(7)	1.990(3)	V(13)–O(7)	1.961(3)
As(8)–O(18)	1.784(3)	V(7)–O(36)	1.622(3)	V(13)–O(12)	1.964(3)
As(8)–O(7)	1.790(3)	V(7)–O(19)	1.940(3)	V(13)–O(27)	1.966(3)
V(1)–O(38)	1.602(3)	V(7)–O(21)	1.946(3)	V(13)–O(22)	1.969(2)
V(1)–O(1)	1.938(3)	V(7)–O(41)	1.975(2)	V(14)–O(8)	1.594(3)
V(1)–O(5)	1.939(3)	V(7)–O(28)	1.990(3)	V(14)–O(21)	1.933(3)
V(1)–O(13)	1.989(3)	V(8)–O(11)	1.602(2)	V(14)–O(14)	1.934(3)
V(1)–O(23)	2.025(3)	V(8)–O(19)	1.939(3)	V(14)–O(28)	1.981(3)
V(2)–O(34)	1.621(3)	V(8)–O(21)	1.940(3)	V(14)–O(31)	1.992(3)
V(2)–O(29)	1.923(2)	V(8)–O(10)	1.982(3)		
V(2)–O(14)	1.935(3)	V(8)–O(20)	1.999(3)		

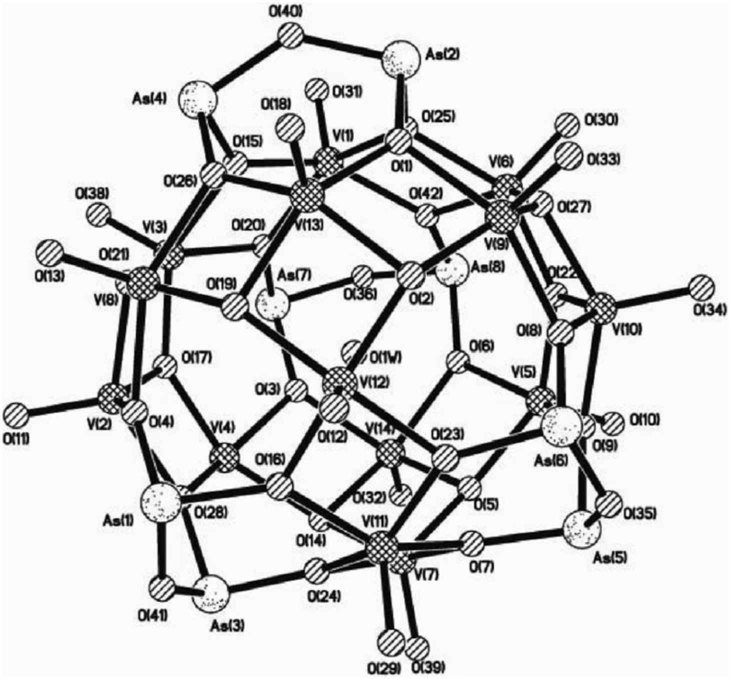

Figure 1. The structure of the $[As_8V_{14}O_{42}H_2O)]^{4-}$ anion in **1**.

In **1**, $[Co(C_4H_{13}N_3)_2]^{2+}$ cations serve as the charge-compensation components. As shown in figure 2, the structure of $[Co(C_4H_{13}N_3)_2]^{2+}$ cations can be easily understood. Each Co^{2+} is coordinated by two diethylenetriamine molecules and Co–N bond distances are between 2.134(8) and 2.212(9) Å. Interestingly, the polyanions are connected through van der Waals forces to generate the soft channels shown in figure 3; the $[Co(C_4H_{13}N_3)_2]^{2+}$ cations and water molecule fill space in the soft channels.

The protonated ethylenediamine is cation in **2** and ethylenediamine and water molecules link different cluster anions to form a supramolecular assembly through

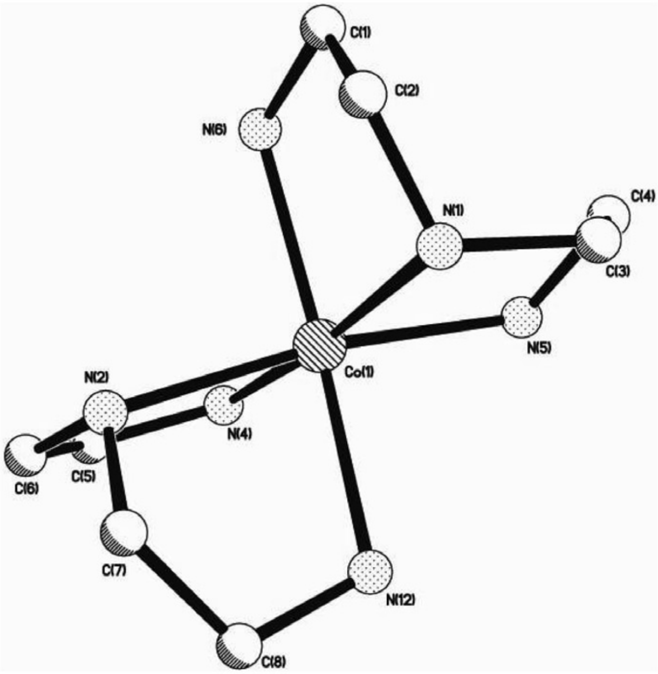

Figure 2. The structure of $[Co(C_4H_{13}N_3)_2]^{2+}$ cations in **1**.

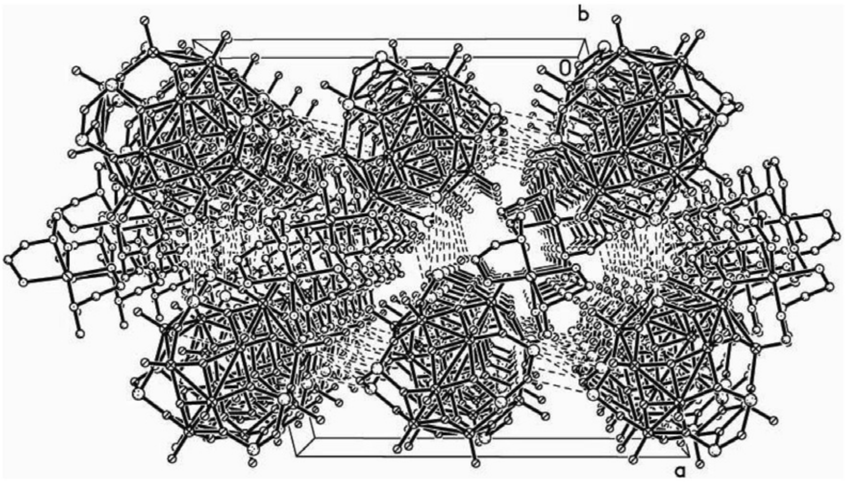

Figure 3. View of crystal packing of **1** along the *b*-axis.

hydrogen bonding [O(2w) $\cdots$ O39($z, x, y-2$), 2.98(2); O(2w) $\cdots$ O42($x, y, z-1$), 2.86(2); O(3w) $\cdots$ O4($0.5+z, -0.5+y, -1.5+z$), 2.92(2); O(3w) $\cdots$ O29($0.5+z, -0.5+y, -1.5+z$), 2.89(2); O(2w) $\cdots$ O(3w), 3.07(2); O(3w) $\cdots$ N6($1+z, x, y-2$), 3.23(2); O(2w) $\cdots$ N6, 2.92(2) Å] (figure 4).

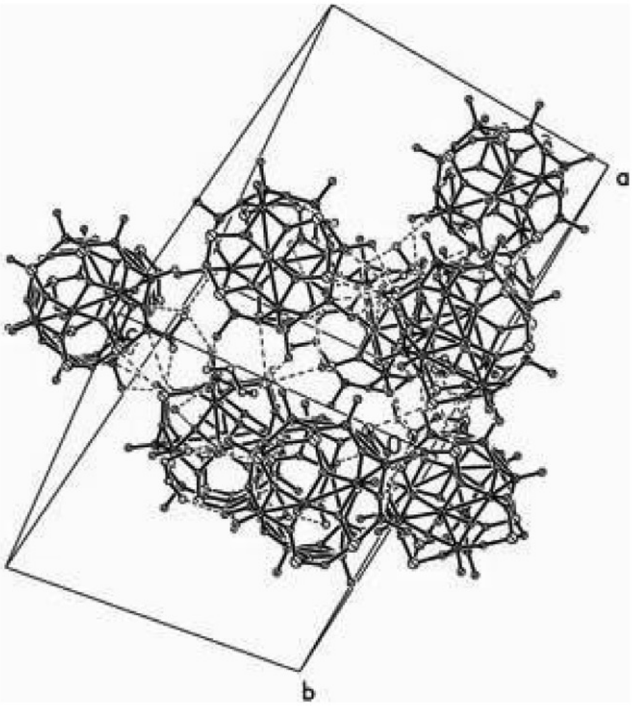

Figure 4. View of crystal packing of **2** along the 110 direction.

The assignment of oxidation for V and As atoms for both compounds are based on bond valence sum calculations [34], which gives the average oxidation of +4 for V and +3 for As. The calculation is in agreement with the formulas of **1** and **2**.

The IR spectrum of **1** exhibits two intense bands, $983\,\mathrm{cm}^{-1}$ is due to the terminal V = O stretching and $556–759\,\mathrm{cm}^{-1}$ are attributed to υ(M–O–M) (M = As, V) and υ(As–O). Absorptions around 3443, 3322, and $2924\,\mathrm{cm}^{-1}$ are characteristic of NH_2 and CH_2.

The IR spectrum of **2** exhibits the characteristic band at $985\,\mathrm{cm}^{-1}$ for terminal V = O stretching and at 827, 754, and $707\,\mathrm{cm}^{-1}$ for V–O–V.

Thermogravimetric (TG) analyses were carried out under N_2 from 50 to 800°C at a heating rate of $10^{\circ}\mathrm{C\,min}^{-1}$ for **1** and **2**. The TG curve of **1** (figure 5a) can be divided into three stages: The first occurs between 50 and 270°C with a weight loss of 2.5%; The second weight loss is 16.3%, from 270 to 500°C; Finally a weight loss of 34.2% in the temperature range 500–800°C. The observed values agree with the calculated value for crystallizing water (2.43%), diethylenetriamine (15.90%) and sublimation of As_2O_3 and structural water (31.17%).

The TGA of **2** (figure 5b) reveals a weight loss of 1.89% between 50 and 210°C, followed by a further weight loss of 8.45% between 210 and 487°C, and finally a weight loss of 38.70% from 487 to 800°C. The calculated weight losses for crystallizing water (1.87%), ethylenediamine (8.00%), and sublimation of As_2O_3 and structural water (36.31%) are in agreement with these results.

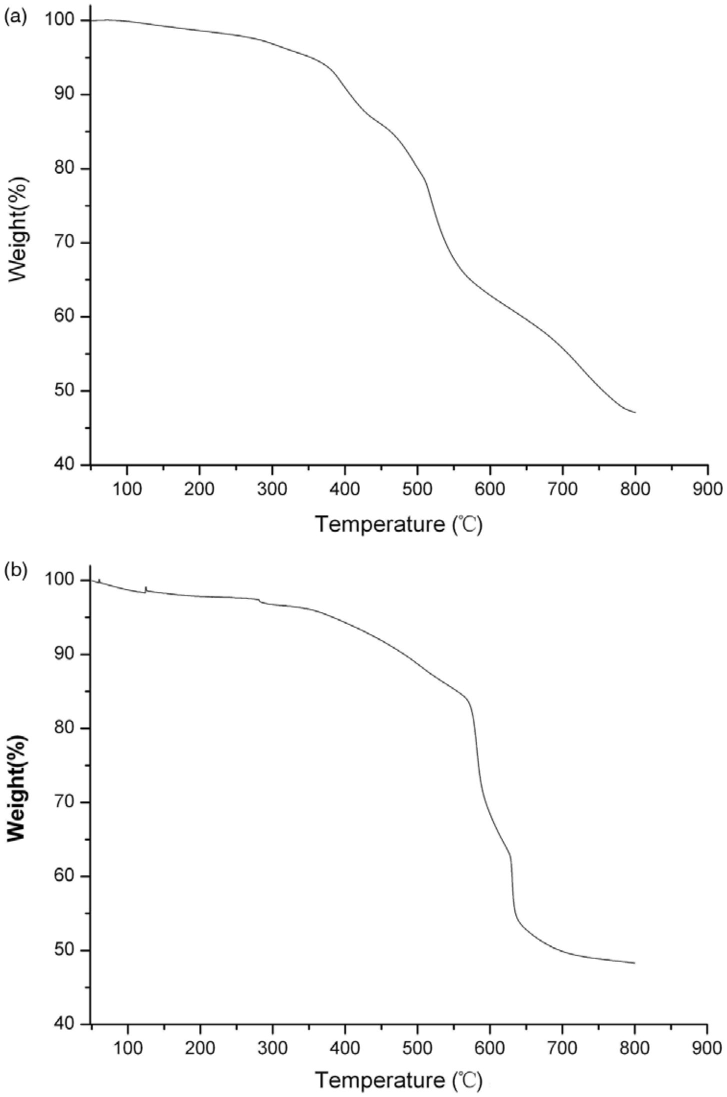

Figure 5. (a) TG curve of **1**. (b) TG curve of **2**.

In summary, two new arsenic–vanadate compounds, **1** and **2**, have been hydrothermally synthesized and their structures characterized by single crystal X-ray diffraction, IR and TG analysis. The polyanions of **1** are connected through van der Waals forces to generate soft channels that are filled by $[Co(C_4H_{13}N_3)_2]^{2+}$.

Acknowledgement

The authors thank the Nature Science Foundation of Liaoning province (20062139) for financial support.

References

[1] P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem. Int. Ed.*, **38**, 2638 (1999).
[2] A. Müller, H. Reuter, S. Dillinger. *Angew. Chem., Int. Ed. Engl.*, **34**, 2328 (1995).
[3] A. Müller, F. Peters, M.T. Pope, D. Gatteschi. *Chem. Rev.*, **98**, 239 (1998).
[4] P.V. Braun, P. Osenar, V. Tohver, S.B. Kennedy, S.I. Stupp. *J. Am. Chem. Soc.*, **121**, 7302 (1999).
[5] A. Müller, J. Döring. *Z. Anorg. Allg. Chem.*, **595**, 251 (1991).
[6] G. Huan, M.A. Greaney, A.J. Jacobson. *J. Chem. Soc., Chem. Commun.*, **4**, 260 (1991).
[7] W. Bu, L. Ye, G. Yang, M. Shao, Y. Fan, J. Xu. *Chem. Commun.*, 1279 (2000).
[8] Y. Li, G. De, M. Yuan, E. Wang, R. Huang, C. Hu, N. Hu, H. Jia. *Dalton Trans.*, 331 (2003).
[9] A. Müller, M. Penk, J. Döring. *Inorg. Chem.*, **30**, 4935 (1991).
[10] R.C. Haushalter, Z. Wang, L.M. Meyer, S.S. Dhingra, M.E. Thompson, J. Zubieta. *Chem. Mater.*, **6**, 1463 (1994).
[11] L.H. Huang, H.M. Kao, K.H. Lii. *Inorg. Chem.*, **41**, 2936 (2002).
[12] A. Müller, J. Döring, H. Bögge. *J. Chem. Soc., Chem. Commun.*, **5**, 273 (1991).
[13] E. Dumas, C. Livage, S. Halut, G. Hervé. *Chem. Commun.*, 2437 (1996).
[14] A. Müller, J. Döring. *Angew. Chem., Int. Ed. Engl.*, **27**, 1721 (1988).
[15] Y. Hou, Y. Wei, D. Xiao, E. Shen, E. Wang, Y. Li, L. Xu, C. Hu. *Inorg. Chim. Acta*, **357**, 2477 (2004).
[16] S. Zheng, J. Zhang, G. Yang. *Chem. Lett.*, **32**, 810 (2003).
[17] S. Zheng, Y. Chen, J. Zhang, G. Yang. *Z. Anorg. Allg. Chem.*, **632**, 155 (2006).
[18] W. Bu, G. Yang, L. Ye, J. Xu, Y. Fan. *Chem. Lett.*, **5**, 462 (2000).
[19] S. Zheng, J. Zhang, G. Yang. *Z. Anorg. Allg. Chem.*, **631**, 170 (2005).
[20] A.L. Barra, D. Gatteschi, B.S. Tsukerblatt, J. Döring, A. Müller, L.C. Brunel. *Inorg. Chem.*, **31**, 5132 (1992).
[21] Y. Xu, H. Zhu, H. Cai, X. You. *Chem. Commun.*, 787 (1999).
[22] Y. Xu, J. Xu, G. Yang, T. Wang, Y. Xing, Y. Ling, H. Jia. *Polyhedron*, **17**, 2441 (1998).
[23] Y. Xu, D. Zhu, Z. Guo, Y. Shi, K. Zhang, X. You. *Dalton Trans.*, 772 (2001).
[24] Y. Xu, D. Zhu, Y. Song, X. Zheng, X. You. *J. Mol. Struct.*, **782**, 165 (2006).
[25] Y. Xu, L. Nie, G. Zhang, Q. Chen, X. Zheng. *Inorg. Chem. Commun.*, 329 (2006).
[26] M.I. Khan, Q. Chen, J. Zubieta. *Inorg. Chim. Acta*, **212**, 199 (1993).
[27] X. Cui, J. Xu, Y. Li, Y. Sun, L. Ye, G. Yang. *J. Mol. Struct.*, **657**, 397 (2003).
[28] X. Cui, Y. Sun, G. Yang. *Inorg. Chem. Commun.*, **6**, 259 (2003).
[29] X. Cui, J. Xu, Y. Li, Y. Sun, G. Yang. *Eur. J. Inorg. Chem.*, 1051 (2004).
[30] S. Zheng, J. Zhang, G. Yang. *J. Mol. Struct.*, **705**, 127 (2004).
[31] C. Wang, Q. Zeng, J. Zhang, G. Yang. *J. Clust. Sci.*, **16**, 65 (2005).
[32] S. Zheng, J. Xu, G. Yang. *J. Clust. Sci.*, **16**, 23 (2005).
[33] G.M. Sheldrick. *SHELXTL Version 5.10*, Bruker AXS Inc., Madison, Wisconsin, USA (1997).
[34] I.D. Brown, D. Altermatt. *Acta Crystallogr. Sect. B*, **41**, 240 (1985).