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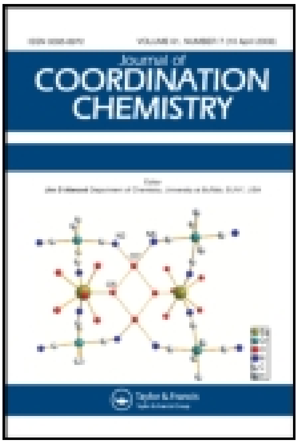

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Hydrothermal synthesis, characterization, and luminescence of two new arsenic-vanadium compounds with a γ-$[As_8V_{14}O_{42}(H_2O)]^{4-}$ anion

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Hydrothermal synthesis, characterization, and luminescence of two new arsenic–vanadium compounds with a γ-$[As_8V_{14}O_{42}(H_2O)]^{4-}$ anion

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Two new compounds, $[Zn(phen)_3]_2[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]\cdot 4H_2O$ (**1**) and $[Cd(phen)_3]_2[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]\cdot 2H_2O$ (**2**) (phen = 1,10′-phenanthroline), have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction, infrared spectrum, and thermogravimetric analysis. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.429(4)$ Å, $b = 15.760(5)$ Å, $c = 15.952(5)$ Å, $\alpha = 108.825(5)^\circ$, $\beta = 92.194(5)^\circ$, $\gamma = 104.155(5)^\circ$, $V = 2615.6(15)$ Å^3, $Z = 1$; **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.450(4)$ Å, $b = 15.629(6)$ Å, $c = 16.302(6)$ Å, $\alpha = 109.177(5)^\circ$, $\beta = 92.628(5)^\circ$, $\gamma = 104.251(4)^\circ$, $V = 2644.8(17)$ Å^3, $Z = 1$. Single-crystal structural analysis shows that both **1** and **2** consist of a new type of $[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]^{4-}$ cluster anion.

Keywords: Arsenic–vanadate; $[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]^{4-}$; Hydrothermal synthesis; Crystal structure

1. Introduction

Attention has focused on V–O clusters for their potential applications in electrochemistry, catalysis, selective adsorption, and photochemistry [1–4]. Various V–O clusters have been reported [5–9], one of which is an arsenic–vanadate compound. Structurally determined As–V compounds with 0-D, 1-D, 2-D, and 3-D structures have been reported, such as $[As_2V_{10}O_{26}(H_2O)]\cdot 8H_2O$ [10], $[Cu(phen)]_2[V_5As_2O_{19}]\cdot 0.5H_2O$ [11], $[NBu_4]_4[As_8V_6O_{26}]$ [12], etc. [13–27]. Since the first report of $[As_8V_{14}O_{42}]^{4-}$ in 1991, some As–V clusters with $[As_8V_{14}O_{42}]^{4-}$ have been prepared, including $[As_8V_{14}O_{42}(X)]^{n-}$ ($X = Cl^-$; CO_3^{2-}; PO_4^{3-}) [28–30] and $[As_8V_{14}O_{42}(SO_4)]^{6-}$ [31, 32]; all these arsenic–vanadium compounds were determined to have α-$[As_8V_{14}O_{42}]^{4-}$ or β-$[As_8V_{14}O_{42}]^{4-}$ cluster anion [33–38]. Here we synthesized two new

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arsenic–vanadium compounds, $[Zn(phen)_3]_2[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]\cdot 4H_2O$ (**1**) and $[Cd(phen)_3]_2[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]\cdot 2H_2O$ (**2**), both of which consist of a new type of cluster anion, $[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]^{4-}$.

2. Experimental

2.1. *Materials and methods*

All starting chemicals were commercially available and used without purification. C, H, and N analyses were carried out on a Perkin-Elmer 240 C elemental analyzer. Infrared (IR) spectra were recorded on a Bruker Optik Gmbh spectrophotometer from 400 to 4000 cm^{-1} as KBr pellets. Thermogravimetric (TG) analysis was carried out on a Diamond TG/DTA instrument (Perkin-Elmer) from 50°C to 1000°C under N_2 at a heating rate of 10°C min^{-1}.

2.2. *Syntheses of the complexes*

2.2.1. $[Zn(phen)_3]_2[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]\cdot 4H_2O$. A mixture of As_2O_3 (0.30 g), V_2O_5 (0.18 g), $Zn(OAc)_2\cdot 6H_2O$ (0.26 g), phen (0.2 g), diethylenetriamine (0.22 g), and H_2O (10.01 g) in 1.5 : 1 : 1 : 1 : 2 : 556 molar ratio was stirred for 50 min in air, then transferred and sealed in an 18 mL Teflon-lined autoclave, and kept at 453 K under autogenous pressure for 3 days. After cooling to room temperature, filtering off, and washing with water, brown block crystals were obtained (0.29 g, yield 61.7% based on vanadium). Analysis found (%): C, 26.26; N, 5.09; H, 1.72 (Calcd (%): C, 26.29; N, 5.11; H, 1.76).

2.2.2. $[Cd(phen)_3]_2[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]\cdot 2H_2O$. A mixture of As_2O_3 (0.20 g), V_2O_5 (0.18 g), $Cd(OAc)_2\cdot 6H_2O$ (0.27 g), phen (0.2 g), diethylenetriamine (0.21 g), and H_2O (8.03 g) in 1 : 1 : 1 : 1 : 2 : 446 molar ratio was stirred for 1 h in air, then transferred and sealed in an 18 mL Teflon-lined autoclave, and kept at 423 K under autogenous pressure for 5 days. After cooling to room temperature, filtering off, and washing with water, brown block crystals were obtained (0.3 g, yield 62.8% based on vanadium). Analysis found (%): C, 25.86; N, 5.07; H, 1.64 (Calcd (%): C, 25.83; N, 5.02; H, 1.61).

2.3. *X-ray crystallography*

Single crystals of both compounds were mounted onto a thin glass fiber by epoxy glue in air for data collection. Diffraction data were collected with a Bruker Apex II CCD with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K using ω–2θ scan method. An empirical absorption correction was applied. All non-hydrogen atoms were refined anisotropically, while hydrogens in organic molecules of the two compounds were refined in calculated positions, assigned isotropic thermal parameters, and allowed to ride on their parent atoms. Hydrogens of water are located in difference maps. All calculations were performed using the SHELX97 program package. Crystal data are presented in table 1 and selected bond lengths are listed in tables 2 and 3.

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

Compound	**1**	**2**
Empirical formula	$C_{72}H_{58}As_8N_{12}O_{47}V_{14}Zn_2$	$C_{72}H_{54}As_8N_{12}O_{45}V_{14}Cd_2$
Formula weight ($g\,mol^{-1}$)	3286.56	3344.59
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	11.429(4)	11.450(4)
b	15.760(5)	15.629(6)
c	15.952(5)	16.302(6)
α	108.825(5)	109.177(5)
β	92.194(5)	92.628(5)
Γ	104.155(5)	104.251(4)
Volume (Å^3), Z	2615.6(15), 1	2644.8(17), 1
Calculated density ($g\,cm^{-3}$)	2.087	2.100
Absorption coefficient, μ (mm^{-1})	4.240	4.139
F (000)	1596	1612
Crystal size (mm^3)	$0.11 \times 0.10 \times 0.07$	$0.12 \times 0.12 \times 0.08$
θ range for data collection (°)	1.85–24.71	1.85–25.50
Limiting indices	$-13 \le h \le 12$; $-14 \le k \le 18$; $-18 \le l \le 17$	$-13 \le h \le 11$; $-16 \le k \le 18$; $-19 \le l \le 16$
Reflections collected/unique	12,958	13,855
Independent reflection	8807 [R(int) = 0.0591]	9645 [R(int) = 0.0364]
Max. and min. transmission	0.7556 and 0.6527	0.7330 and 0.6365
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/parameters	8807/806	9645/775
Goodness-of-fit on F^2	1.081	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0708$, $wR_2 = 0.1255$	$R_1 = 0.0670$, $wR_2 = 0.1865$
R indices (all data)	$R_1 = 0.1614$, $wR_2 = 0.1551$	$R_1 = 0.1013$, $wR_2 = 0.2058$

3. Results and discussion

3.1. *Crystal structures*

Single crystal structural analysis reveals that **1** consists of a new type $[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]^{4-}$ anion, $[Zn(phen)_3]^{2+}$, and waters of crystallization. $\alpha\text{-}[As_8V_{14}O_{42}]^{4-}$ and $\beta\text{-}[As_8V_{14}O_{42}]^{4-}$ polyanions have been reported previously. Both $\alpha\text{-}[As_8V_{14}O_{42}]^{4-}$ and $\beta\text{-}[As_8V_{14}O_{42}]^{4-}$ are constructed from four As_2O_5 moieties with 14 distorted VO_5 square pyramids [28–38]. Compared with $\alpha\text{-}[As_8V_{14}O_{42}]^{4-}$, the difference is that half of the $\beta\text{-}[As_8V_{14}O_{42}]^{4-}$ shell is rotated by 90° around its S4 axes. As shown in figure 1, $[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]^{4-}$ in **1** can be divided into two parts: half occupied α- and $\beta\text{-}[As_8V_{14}O_{42}(H_2O)]^{4-}$ cluster anions. Eight vanadium [V_2, V_3, V_4, V_5, V_{2A}, V_{3A}, V_{4A}, V_{5A} (A: $1-x$, $-y$, $1-z$)] oxygen square pyramids (VO_5) connect to each other by sharing bridging oxygens, forming a central V_8 belt, in which the eight vanadiums approximately form a regular octagon. The V–V–V angles are between 136.16(15) and 138.35(9)°, while V–V distances vary from 3.0121(17) to 3.0418(17) Å in the V_8 belt, as found in the reported α- and β-type $[As_8V_{14}O_{42}]^{4-}$ [22, 29, 30, 38]. In both structures of α- and β-type $[As_8V_{14}O_{42}]^{4-}$, two handle-like As_2O_5 building units and one V_3O_7

Table 2. Selected bonds distances (Å) for **1**.

V(1)–O(15)	1.591(4)	V(5)–O(13)	1.957(4)	As(1)–O(21)	1.849(3)
V(1)–O(18)	1.935(4)	V(5)–O(2)#1	1.969(4)	As(1)–O(9)	1.857(4)
V(1)–O(16)	1.965(3)	V(6)–O(4)	1.533(3)	As(2)–O(18)	1.711(4)
V(1)–O(14)	1.974(4)	V(6)–O(2)	1.872(4)	As(2)–O(6)	1.881(4)
V(1)–O(5)	1.983(4)	V(6)–O(11)	1.894(4)	As(2)–O(21)	1.991(4)
V(2)–O(19)	1.588(4)	V(6)–O(16)	2.097(4)	As(3)–O(5)	1.707(4)
V(2)–O(10)	1.957(4)	V(6)–O(14)	2.104(3)	As(3)–O(17)	1.869(4)
V(2)–O(11)#1	1.959(4)	V(7)–O(20)	1.523(3)	As(3)–O(7)	1.951(4)
V(2)–O(9)#1	1.966(3)	V(7)–O(13)	1.832(4)	As(4)–O(14)	1.693(4)
V(2)–O(17)	1.966(4)	V(7)–O(10)	1.857(4)	As(4)–O(1)	1.852(4)
V(3)–O(8)	1.591(4)	V(7)–O(18)	2.152(4)	As(4)–O(7)	1.886(3)
V(3)–O(6)#1	1.942(3)	V(7)–O(5)	2.156(4)	As(5)–O(14)	1.731(4)
V(3)–O(9)#1	1.961(4)	V(8)–O(21)	1.523(3)	As(5)–O(4)	1.837(4)
V(3)–O(1)	1.967(4)	V(8)–O(9)	1.862(3)	As(5)–O(2)	1.923(4)
V(3)–O(17)	1.968(3)	V(8)–O(6)	1.951(4)	As(6)–O(5)	1.646(4)
V(4)–O(12)	1.597(4)	V(8)–O(16)	2.086(4)	As(6)–O(10)	1.925(4)
V(4)–O(13)#1	1.944(4)	V(8)–O(18)	2.123(4)	As(6)–O(20)	1.939(4)
V(4)–O(6)#1	1.954(4)	V(9)–O(7)	1.523(3)	As(7)–O(16)	1.732(4)
V(4)–O(2)	1.961(4)	V(9)–O(1)	1.863(4)	As(7)–O(4)	1.881(4)
V(4)–O(1)	1.969(3)	V(9)–O(17)	1.959(5)	As(7)–O(11)	1.932(4)
V(5)–O(3)	1.608(4)	V(9)–O(14)	2.083(4)	As(8)–O(18)	1.688(4)
V(5)–O(11)#1	1.953(4)	V(9)–O(5)	2.127(4)	As(8)–O(20)	1.845(4)
V(5)–O(10)	1.957(4)	As(1)–O(16)	1.689(4)	As(8)–O(13)	1.941(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y$, $-z+1$.

Table 3. Selected bonds distances (Å) for **2**.

V(1)–O(15)	1.570(4)	V(5)–O(2)#1	1.961(4)	As(1)–O(21)	1.858(4)
V(1)–O(18)	1.954(4)	V(5)–O(11)#1	1.963(4)	As(1)–O(9)	1.864(4)
V(1)–O(14)	1.960(4)	V(6)–O(4)	1.526(4)	As(2)–O(18)	1.704(4)
V(1)–O(16)	1.967(3)	V(6)–O(2)	1.867(4)	As(2)–O(6)	1.867(4)
V(1)–O(5)	1.988(4)	V(6)–O(11)	1.888(4)	As(2)–O(21)	1.987(4)
V(2)–O(19)	1.605(4)	V(6)–O(16)	2.095(4)	As(3)–O(5)	1.724(4)
V(2)–O(11)#1	1.953(4)	V(6)–O(14)	2.102(4)	As(3)–O(17)	1.876(4)
V(2)–O(10)	1.956(4)	V(7)–O(20)	1.522(3)	As(3)–O(7)	1.943(5)
V(2)–O(17)	1.969(4)	V(7)–O(13)	1.824(5)	As(4)–O(14)	1.716(4)
V(2)–O(9)#1	1.972(3)	V(7)–O(10)	1.881(4)	As(4)–O(1)	1.847(4)
V(3)–O(8)	1.609(4)	V(7)–O(5)	2.116(5)	As(4)–O(7)	1.865(4)
V(3)–O(6)#1	1.941(3)	V(7)–O(18)	2.135(4)	As(5)–O(14)	1.726(4)
V(3)–O(17)	1.950(4)	V(8)–O(21)	1.522(3)	As(5)–O(4)	1.807(4)
V(3)–O(9)#1	1.966(4)	V(8)–O(9)	1.882(3)	As(5)–O(2)	1.953(4)
V(3)–O(1)	1.975(4)	V(8)–O(6)	1.907(5)	As(6)–O(5)	1.652(4)
V(4)–O(12)	1.595(4)	V(8)–O(18)	2.109(4)	As(6)–O(10)	1.912(5)
V(4)–O(2)	1.950(4)	V(8)–O(16)	2.109(5)	As(6)–O(20)	1.937(4)
V(4)–O(13)#1	1.956(4)	V(9)–O(7)	1.522(3)	As(7)–O(16)	1.704(4)
V(4)–O(1)	1.967(3)	V(9)–O(1)	1.883(4)	As(7)–O(4)	1.903(5)
V(4)–O(6)#1	1.968(4)	V(9)–O(17)	1.915(5)	As(7)–O(11)	1.938(4)
V(5)–O(3)	1.600(4)	V(9)–O(14)	2.107(4)	As(8)–O(18)	1.719(4)
V(5)–O(13)	1.946(4)	V(9)–O(5)	2.145(4)	As(8)–O(20)	1.812(4)
V(5)–O(10)	1.955(5)	As(1)–O(16)	1.712(4)	As(8)–O(13)	1.948(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y$, $-z+1$.

fragment are linked by bridging oxygens above and below this V_8 belt. In $[\gamma\text{-}As_8V_{14}O_{42}]^{4-}$, V6, V7, V8, V9, and all As are disordered with occupation factors of 0.5. Therefore, four half-occupied handle-like As_2O_5 building units and two V_3O_7 fragments are linked to each other and attached above and below the V_8 belt, as shown

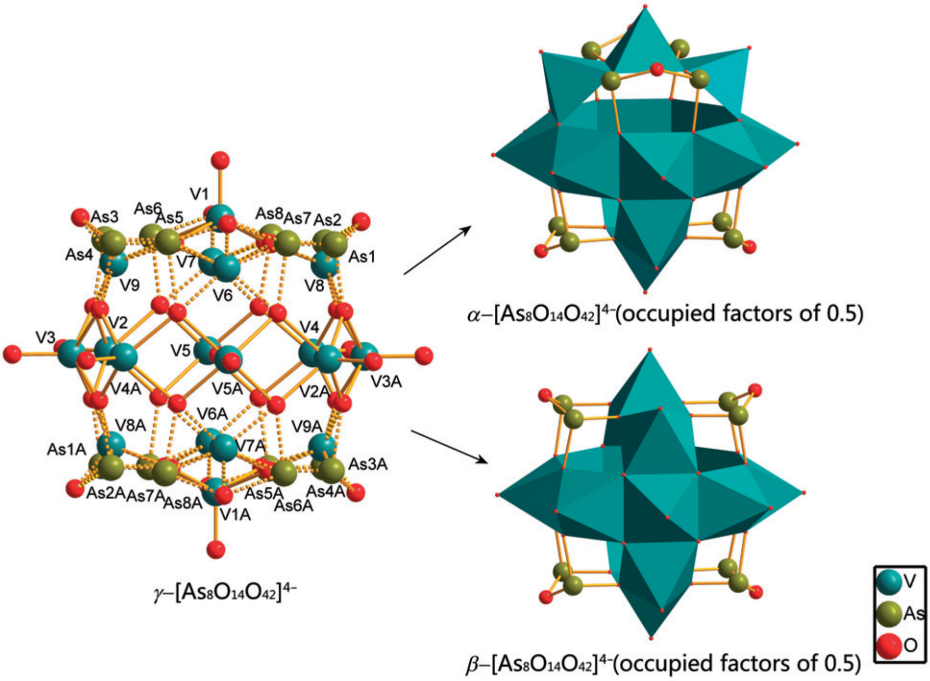

Figure 1. The ball-and-stick and polyhedral structures of the polyoxoanions. The bonds of As or V and O, presented by dotted lines, are disordered with occupation factors of 0.5. Hydrogens are omitted for clarity.

in figure 1. Although the components of α-, β-, and γ-type $[As_8V_{14}O_{42}]^{4-}$ polyanions are the same, the structures are different. γ-type $[As_8V_{14}O_{42}]^{4-}$ can be described as a mixture of α- and β-$[As_8V_{14}O_{42}]^{4-}$ with the occupation factors of 0.5. The bond distances of V–O are 1.563(9)–1.634(8) Å for V–Ot and 1.873(8)–2.052(9) Å for V–Ob, while the As–O bond lengths are between 1.616(3) and 2.021(2) Å. O–V–O angles range from 75.34(17) to 146.2(2)°, while O–As–O angles vary from 95.10(16) to 108.36(19)°. These distances and angles are similar to those found in other As–V compounds [22–40]. O1w is located in the symmetry center (0.5, 0, 0.5) and surrounded by $[\gamma\text{-}As_8V_{14}O_{42}]^{4-}$ anions. As shown in figure 2, adjacent $[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]^{4-}$ anions are connected with each other to generate a $[\gamma - As_8V_{14}O_{42}(H_2O)]_n^{4n-}$ chain, which is further linked by waters using hydrogen bonds to make a supermolecular layer. $[Zn(phen)_3]^{2+}$ fill between the layers. Each Zn^{2+} is coordinated by three phen ligands to generate an octahedron. The Zn–N distances and the N–Zn–N angles are 2.145(4)–2.235(4) Å and 76.5(2)–169.88(18)°, respectively (figure 3).

The assignment of oxidation states for As and V of **1** are based on bond valence sum calculations [41], which give average oxidation of +3 for As and +4 for V, respectively. The calculated value is in agreement with the formula of **1**.

When we replaced $Zn(OAC)_2 \cdot 6H_2O$ by $Cd(OAC)_2 \cdot 6H_2O$ with a slightly different temperature, $[Cd(phen)_3]_2[\gamma\text{-}As_8V_{14}O_{42}(H_2O)] \cdot 2H_2O$ (**2**) was prepared. Both compounds possess the $[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]^{4-}$ anions, while the structure of $[Cd(phen)_3]^{2+}$ cation in **2** is also similar to $[Zn(phen)_3]^{2+}$ in **1**, with the only different crystallization water number.

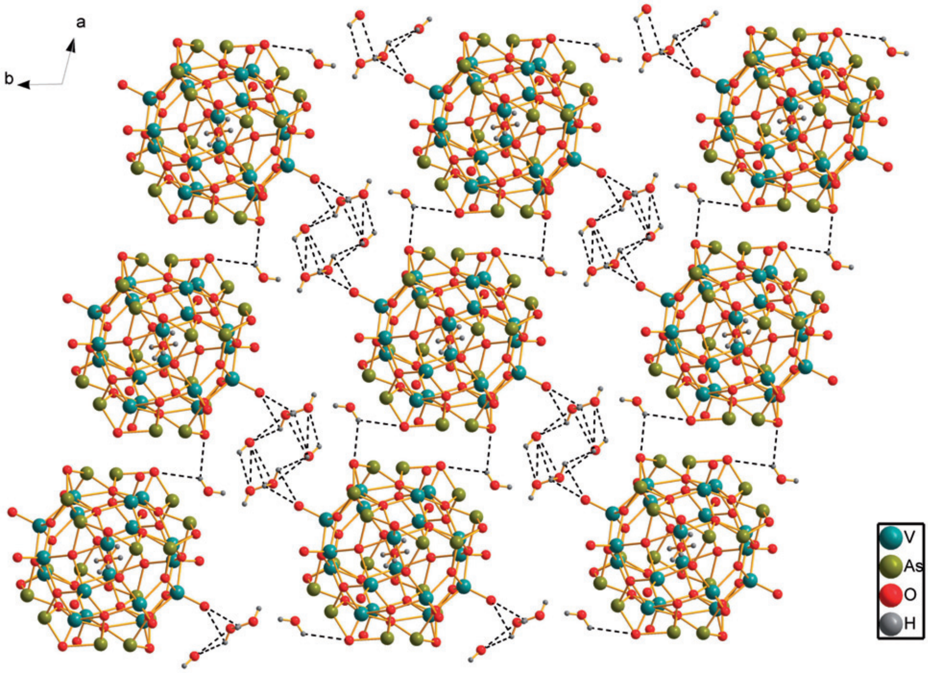

Figure 2. Adjacent γ-$[As_8V_{14}O_{42}]^{4-}$ are connected by hydrogen bonding to make a soft layer.

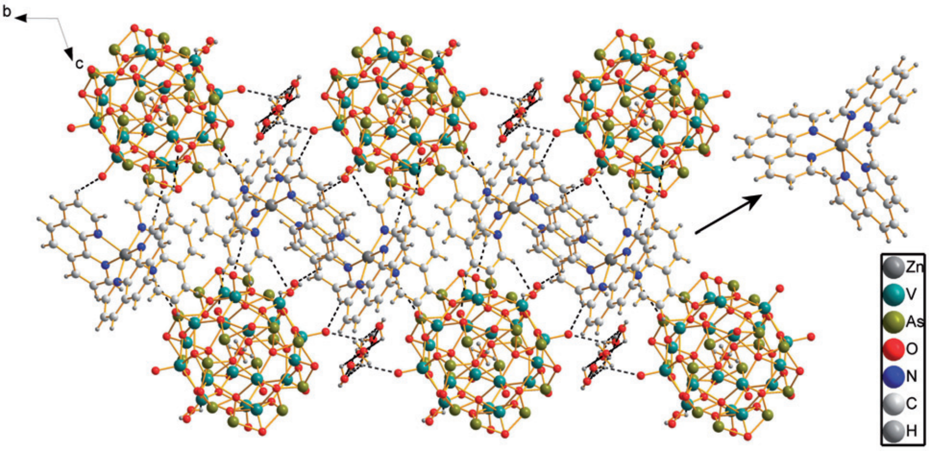

Figure 3. $[Zn(phen)_3]^{2+}$ cations filled by hydrogen bonds between the adjacent polyanion layers.

3.2. *IR spectrum*

In IR spectra, strong bands at 764–559 cm^{-1} for **1** and 764–553 cm^{-1} for **2** are attributed to ν(M–O–M) (M = As, V) and ν(As–O). Bands at 1620–1099 cm^{-1} are attributed to characteristic bands of 1,10-phenanthroline. Bands at 988 and 995 cm^{-1} are due to terminal V=O stretch. Bands at 462 cm^{-1} for **1** and 463 cm^{-1} for **2** are

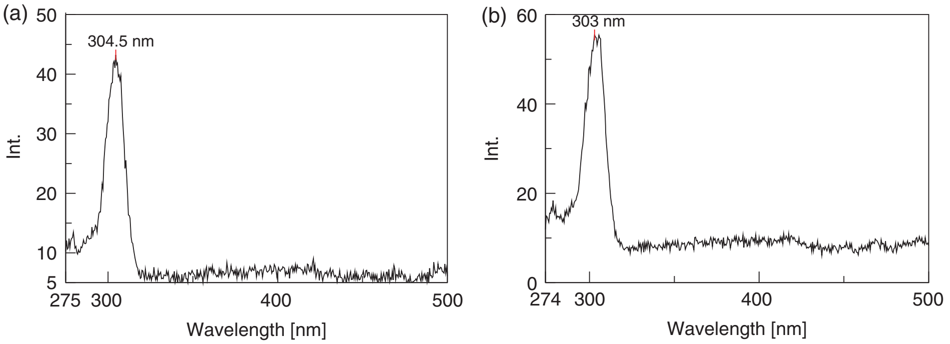

Figure 4. Excitation and emission spectra of **1** (a) and **2** (b).

ascribed to Zn–N and Cd–N bonds. Bands at 3448 and 3452 cm^{-1} for both compounds are associated with the aqua ligands.

3.3. *Optical properties*

Excitation and emission spectra of **1** in the solid state at room temperature are shown in figure 4a. Fluorescence in the UV region for **1** can be observed, where the maximum emission wavelength is 304.5 nm. Correspondingly, the peak with maximum excited light at *ca* 265 nm can be observed in excitation spectra. The enhanced fluorescence efficiency of **1** is attributed to coordination of phen to Zn(II), which effectively increases the rigidity of the ligand and reduces the loss of energy by radiation thermal vibrations. Since **2** is very similar to **1**, its fluorescence property is comparable with **1**, as shown in figure 4b.

3.4. *Thermal analysis*

TG curves of **1** and **2** are shown in Supplementary material. Both compounds display weight loss processes with total weight loss of 57.94% for **1** and 63.72% for **2** from 50°C to 1000 °C, attributed to release of free water (Calcd 2.19% for **1** and 1.08% for **2**), coordinated water (Calcd 0.55% for **1** and 0.54% for **2**) and 1,10-phenanthroline groups (Calcd 32.86% for **1** and 32.29% for **2**), and sublimation of As_2O_3 (Calcd 24.08% for **1** and 23.66% for **2**).

4. Conclusions

Two new compounds, $[Zn(phen)_3]_2[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]\cdot 4H_2O$ (**1**) and $[Cd(phen)_3]_2[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]\cdot 2H_2O$ (**2**), have been synthesized under hydrothermal conditions. Single crystal structural analysis shows that both consist of $[\gamma\text{-}As_8V_{14}O_{42}(H_2O)]^{4-}$ polyanions. The synthesis of the two compounds demonstrates that new As–V–O cluster anions can be synthesized by using different sized cations.

Supplementary material

CCDC-797945 and 797946 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge *via* http://www.ccdc.com.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E2, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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