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A New 2-D Network Containing $\{As_4V_{16}O_{42}(H_2O)\}$ Cluster Units

Jian Zhou,[a] Shou-Tian Zheng,[a] Wei-Hui Fang,[a] and Guo-Yu Yang*[a]

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A new polyoxometalate $[Cd(dien)]_2[Cd(dien)(H_2O)]_2[As_4V_{16}O_{42}(H_2O)]\cdot 2H_2O$ (**1**, dien = diethylenetriamine) has been hydrothermally synthesized and structurally characterized. **1** is the first example of 2-D network based on the linkages of the rare $\{As_4V_{16}O_{42}(H_2O)\}$ cluster units and two types of cadmium(II) complex fragments. The magnetic susceptibility shows the antiferromagnetic interaction between V^{IV} cations in **1**.

Introduction

Polyoxometalates (POM) have provoked significant interest owing to their unique structures and potential applications in catalysis, materials science, medicine, nanotechnology, and magneto-chemistry.[1] Recently, the design and construction of extended POM materials has been made important progress.[2–5] One usual approach is that the POM units are joined by different types of linkers of complex cations, metal cations, or organic ligands. For example, the metal complexes and the metal cations may link POM units to form 1-, 2-, and 3-D structures.[2,3] Lately, we used multicarboxylate likers to join the Ni_6-substituted POM units to produce a series of 1-, 2-, and 3-D organic cluster frameworks.[4] Generally, almost of the extended POM frameworks are joined by the same linkers, while the extended POMs containing different linkers are rare.[5] Therefore, the use of different linkers for making extended POMs is highly challenging.

In POMs family, an important subclass is vanadoarsenates with formula $[As_{2n}V_{18n}O_{42}(X)]^{m-}$ (X = H_2O/Cl/SO_3) derived from the well-known $\{V_{18}O_{42}\}$ cluster shell, which display interesting electronic and magnetic properties.[6] Since the first vanadoarsenate cluster $[As_6V_{15}O_{42}(H_2O)]^{6-}$ was made in 1988,[6a] a large number of vanadoarsenates have been made, such as $Na_4[V^{IV}{}_8V^{V}{}_4As_8O_{40}(H_2O)]\cdot 23H_2O$,[6d] $[M(bbi)_2]_2[As_8V_{14}O_{42}(H_2O)]$ {M = Co/Ni/Zn; bbi = 1,1′-(1,4-butanediyl)bis(imidazole)},[2c] and $[(H_2O)Zn(4,4'\text{-bpy})]_2[As_8V_{14}O_{42}(H_2O)]\cdot 2H_2O$.[7] Recently, we not only made a series of vanadoarsenates with limited aggregate and extended structures linked by transition metal (TM) complexes[8] but also found that the TM ions, such as Ni^{2+}, Zn^{2+} and Cd^{2+}, can substitute one or two VO groups of vanadoarsenate cage to form TM-substituted vanadoarsenates.[5b,9] So far, the cluster shells of vanadoarsenate mainly focus on $[As_6V_{15}O_{42}(X)]$ and $[As_8V_{14}O_{42}(X)]$ moieties. In contrast, $[As_4V_{16}O_{42}(X)]$ moieties are only one example of $[Zn_2(dien)_3]\{[Zn(dien)]_2As_4V_{16}O_{42}(H_2O)\}\cdot 3H_2O$, in which the $\{As_4V_{16}O_{42}(H_2O)\}$ cluster units are linked by dual [Zn(dien)] bridging groups to adopt 1-D structure.[10] As part of our continuing work in this system, herein we report the hydrothermal syntheses and crystal structure of the second novel vanadoarsenate containing $\{As_4V_{16}O_{42}(H_2O)\}$ cluster units, $[Cd(dien)]_2[Cd(dien)(H_2O)]_2[As_4V_{16}O_{42}(H_2O)]\cdot 2H_2O$ (**1**, dien = diethylenetriamine), which not only is the first 2-D vanadoarsenate built by $\{As_4V_{16}O_{42}(H_2O)\}$ cluster, but also contains two different linkers of [Cd(dien)] and $[Cd(dien)(H_2O)]$ fragments.

Results and Discussion

1 was made by hydrothermal reaction of V_2O_5, As_2O_5 and $CdCl_2$ in a mixed solvent of dien and H_2O at 170 °C for 4 days. The starting materials are crucial for the formation of **1**. When As_2O_5 was replaced by As_2O_3 under similar conditions, but no single crystals of **1** were obtained. In our case, the As^V in As_2O_5 as starting materials were reduced to the As^{III} and further form $[As_4V_{16}O_{42}(H_2O)]$ cluster. In addition, both the pH value and reaction temperature of the reaction system are very important for the formation of **1** that was formed at pH 8–9. At lower or higher pH (8 or 9) only black powder of unknown structure was obtained. The crystals of **1** were not also formed when the reaction temperature was adjusted 10 °C above or 20 °C below 170 °C.

Single-crystal structure analysis reveals that **1** has a 2-D layer structure based on the linkages of $[As_4V_{16}O_{42}(H_2O)]$ cluster units and $[Cd(dien)]/[Cd(dien)(H_2O)]$ groups. The $[As_4V_{16}O_{42}(H_2O)]$ cluster is similar to that of $[Zn_2(dien)_3]$-

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[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences,
Fuzhou, Fujian 350002, P. R. China
Fax: +86-591-83710051
E-mail: ygy@fjirsm.ac.cn

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$\{[Zn(dien)]_2As_4V_{16}O_{42}(H_2O)\}\cdot 3H_2O$ reported by our group,[10] which comprises 16 VO_5 square pyramids, 4 AsO_3 trigonal pyramids, and one H_2O molecule located at the centre of the cage (Figure 1, a, b). Two AsO_3 groups are joined together by a μ-O to form an As_2O_5 handle-like unit. Three VO_5 square pyramids share edges to generate an arched V_3O_{11} trimer. Two V_3O_{11} trimers and two As_2O_5 units are alternately joined together via sharing O atoms to form a circular $As_4V_6O_{24}$ unit. Five VO_5 square pyramids share common edges each other to produce the pentanuclear V_5O_{17} fragment. Such two V_5O_{17} fragments further cap to two sides of the $As_4V_6O_{24}$ ring, forming a $[As_4V_{16}O_{42}]^{8-}$ cage with D_{2h} symmetry that can be regarded as that two VO_5 square pyramids of the $[V_{18}O_{42}]$ shell[11] are substituted by two As_2O_5 units. On the basis of valence sum (Σ_s) calculations,[12] the oxidation states of all V and As atoms in **1** are +4 (Σ_s = 4.09–4.18) and +3 (Σ_s = 3.07–3.17), which are consistent with the formula of **1**.

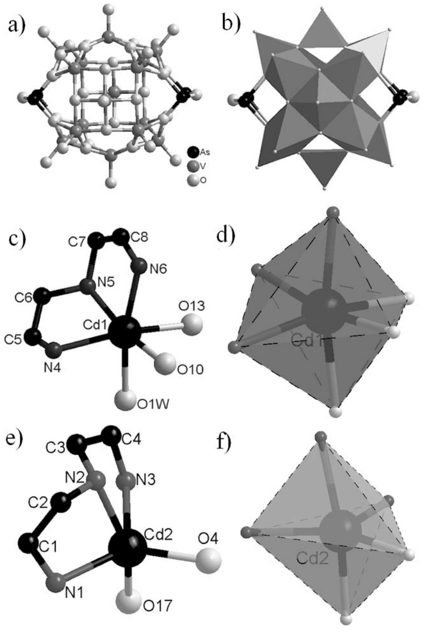

Figure 1. a, b: The ball-and-stick/polyhedral representation of $[As_4V_{16}O_{42}(H_2O)]$ cluster. c, d: The coordination environment of the Cd1 ion. e, f: The coordination environment of the Cd2 ion.

Compared with $[Zn_2(dien)_3]\{[Zn(dien)]_2As_4V_{16}O_{42}(H_2O)\}\cdot 3H_2O$ (**2**),[10] the $[As_4V_{16}O_{42}(H_2O)]$ cluster in **1** acts as an octadentate ligand to bond Cd^{2+} ions, forming a novel 2-D layer (Figure 2, a), while the $[As_4V_{16}O_{42}(H_2O)]$ cluster in **2** only acts as the tetradentate ligand to form 1-D chain. There are two types of Cd^{2+} fragments in **1**: the Cd1 atom is coordinated by one tridentate dien ligand, one water molecule and two O atoms from two adjacent $[As_4V_{16}O_{42}(H_2O)]$ clusters, showing a slightly distorted octahedron (Figure 1, c, d); the Cd2 atom is bonded by one tridentate dien ligand and two O atoms of two adjacent $[As_4V_{16}O_{42}(H_2O)]$ clusters to form a distorted trigonal bipyramidal configuration with the atoms O17 and N2 occupying the axial positions (Figure 1, e, f).

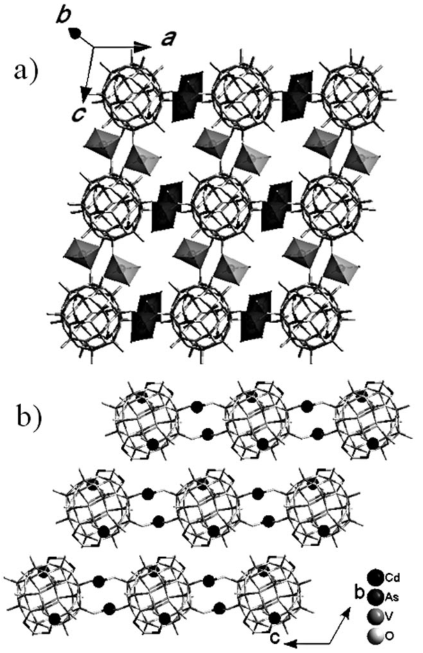

Figure 2. a: View of linkages for the 2-D layer in **1** {color codes: black/grayer, $[Cd(dien)O_2(H_2O)]$/$[Cd(dien)O_2]$ polyhedra}. b: View of the stacking mode for the layers in **1**. The dien ligands have been omitted for clarity.

Another interesting feature of **1** is that the [Cd1(dien)-(H_2O)] and [Cd2(dien)] groups as the bridges always occur in pairs. The $[As_4V_{16}O_{42}(H_2O)]$ units are linked each other by two [Cd1(dien)–(H_2O)] bridges, resulting in an 1-D chain along the *a*-axis. These chains are further interconnected by the [Cd(dien)] bridges along *c*-axis to generate a 2-D neutral layer (Figure 2, a). Such layers are arranged in parallel with an interlayer distance of about 12.97 Å (Figure 2, b). It is noteworthy that the known 2-D layered polyoxovanadates are usually joined by same complex fragments as the single bridges[8a–8b,13] or combination of the single and double bridges.[8c] Only one contains two types of complex fragments as bridges, $[Co(en)_2][Co(bpy)_2]_2[PMo^{VI}{}_5Mo^{V}{}_3V^{IV}{}_8O_{44}]\cdot 4.5H_2O$ (en = ethylenediamine, bpy = 2,2′-bipyridine),[5a] in which the $[Co(bpy)_2]$ and $[Co(en)_2]$ fragments act as the double and single bridges, respectively (see Figure S1, Supporting Information). Therefore, the 2-D layer containing two types of complex fragments as the double bridges is first observed in **1**, to the best of our knowledge.

The topology of the 2-D layer in **1** can be simplified by considering the $[As_4V_{16}O_{42}(H_2O)]$ clusters and [Cd(dien)]/[Cd(dien)(H_2O)] fragments as nodes and linkers, respectively. As a result, a 2-D layer structure of sql topological net with double edges is formed (Figure 3, a). The Schläfli symbol of this net is $4^4\cdot 6^2$. So far, a large number of the sql type nets based on the linkage of one POM (or simple metal) node and six linkers[5a,8c] (Figure 3, b) (or four linkers,[14] Figure 3, c) have been reported, however, the sql type net with double edges (eight linkers) in **1** is rare, mainly because the high connectivity (eight linkers) would like to form the bcc (body-center cubic, normally called the CsCl net)-related type,[15] rather than the sql type. Only one example of pseudo-sql type net is observed in $[Co_3(dca)_6(H_2O)_4]\cdot 2(2,3,5\text{-tmpdo})$ (dca = dicyanamide, 2,3,5-tmpdo = 2,3,5-trimethylpyrazine dioxide), in which two sql type nets are twinned via Co atom.[16] Hence, this special net with double edges in **1** is the first sql net containing $[As_4V_{16}O_{42}(H_2O)]$ cluster as node and mixed complex fragments as double linkers.

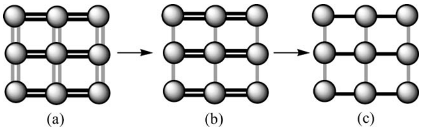

Figure 3. a: The sql topological net with the double edges in **1** {grayer balls, $[As_4V_{16}O_{42}(H_2O)]$ nodes; black/grayer rods, [Cd(dien)]/$[Cd(dien)(H_2O)]$ linkers}. b: The sql topological net with the double edges and single edges in refs.[5a,8f] c: Schematic description of the common sql topological net in ref.[14]

As shown in Figure 4, the IR spectrum of **1** shows that the stretching bands of the $-NH_2$ and $-CH_2$ groups are observed at 3315–3254 and 2926–2871 cm^{-1}, respectively. The bending bands of the $-NH_2$ and $-CH_2$ groups appear at 1593, 1449 and 1394 cm^{-1}, respectively. The occurrence of these resonance signals confirms the presence of amino groups. The broad band at 3432 cm^{-1} can be attributed to O–H stretching. The strong and sharp band at 971 cm^{-1} can be assigned to the stretching vibrations of V=O bonds. A series of bands in the 732–451 cm^{-1} region are characteristic of ν(M–O–M) (M = V or As) and ν(As–O), respectively.

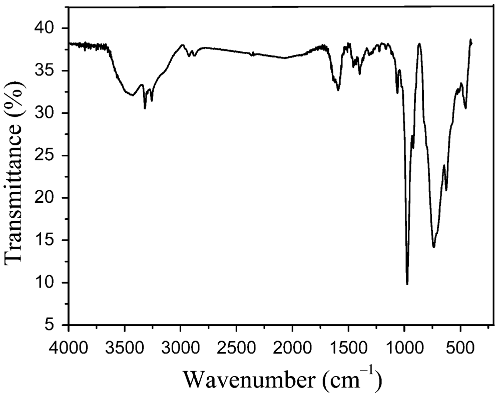

Figure 4. IR spectrum of **1**.

The thermogravimetric study of **1** was carried out in flowing air with a heating rate of 10 °C min^{-1} in the temperature range 30–1000 °C for **1** (Figure S2, Supporting Information). A weight loss of 1.68% occurs from 30 to 170 °C, corresponding to the loss of free water molecules (1.97%). Then, two successive weight losses of 14.77% from 170 to 490 °C was assigned to the removal of coordinated H_2O water molecules and dien ligands, but the observed weight is slightly less than the sum of the calculated weight value (16.38%). This result could be related to the complex weight-loss process from 170 to 490 °C, which includes the weight loss (besides the removal of coordinated H_2O molecules and dien ligands, partial sublimation of As_2O_3 occurs) and weight increase, which is attributed to the partial oxidation of As^{3+} to As^{5+} as well as of the V^{4+} to V^{5+}.[17] The weight increase in the temperature range of 490–550 °C further confirms the oxidation of As^{3+} and V^{4+}. Up to 550 °C for **1**, all of the V^{4+} and the remaining As^{3+} ions are fully oxidated to high-valent oxides of As_2O_5 and V_2O_5. The residual material might be a complex mixture of CdO, V_2O_5 and As_2O_5. The weight of the residue (84.87%) is less than the sum of the calculated weight value (88.66% for 8 V_2O_5, 4 CdO and 2 As_2O_5 per formula unit), which indicates that the partial As_2O_3 was not oxidized to As_2O_5 and in deed sublimated in this process.

The variable-temperature magnetic susceptibility of **1** was measured between 2 and 300 K. The product of $\chi_M T$ decreases smoothly from 2.87 cm^3 mol^{-1} K at 300 K to 0.22 cm^3 mol^{-1} K at 2 K (Figure S3a, Supporting Information). The $\chi_M T$ value of 2.87 cm^3 mol^{-1} K at 300 K is much lower than the expected value for the sixteen uncoupled $S = 1/2$ spins of V^{4+} ions (4.46 cm^3 mol^{-1} K, $g = 2.0$ for V^{4+}), indicating the presence of antiferromagnetic exchange interactions between V^{4+} ions in the $[As_4V_{16}O_{42}(H_2O)]^{8-}$ cluster. Moreover, the plot of χ_M^{-1} vs. T in the range of 300–40 K (Figure S3b, Supporting Information) is well described by the Curie–Weiss law with Curie constant C = 5.76 cm^3 mol^{-1} K and Weiss constant $\theta = -301.0$ K, which further con-firms the occurrence of strong antiferromagnetic exchange interactions between the V^{4+} ions. Such a strong antiferromagnetic coupling can be observed in many polyoxovanadate clusters.[8,9]

Conclusions

In this paper, one new organic-inorganic As–V–O cluster has been hydrothermally made methods and structurally characterized, which provides the first example of 2-D POM constructed from the rare $\{As_4V_{16}O_{42}(H_2O)\}$ cluster units and two types of metal complex fragments as the double bridges. This result demonstrates that the combination of the $\{As_4V_{16}O_{42}(H_2O)\}$ units and different linkers may realize the design of high-dimensional POM materials with potential catalytic, adsorption, and magnetic properties. Further work is in progress.

Experimental Section

Synthesis and Characterization: A mixture of V_2O_5 (0.181 g, 1.0 mmol), As_2O_5 (0.115 g, 0.5 mmol), $CdCl_2\cdot 2.5H_2O$ (0.288 g, 1.0 mmol), dien (0.3 mL) and H_2O (5 mL), was stirred under ambient conditions. The final mixture was sealed in a Teflon-lined steel autoclave and heated at 170 °C for 4 d, and then cooled to room temperature. The black blocks crystals were collected by filtration, washed with distilled water and dried in air (50.3% yield based on As_2O_5). $C_{16}H_{62}As_4Cd_4N_{12}O_{47}V_{16}$: C 7.02, H 2.28, N 6.14; found C 7.11, H 2.35, N 6.06.

X-ray Crystallography: $\{[Cd(dien)]_2[Cd(dien)(H_2O)]_2As_4V_{16}O_{42}(H_2O)\}\cdot 2H_2O$ (**1**): triclinic, space group $P\bar{1}$, a = 12.894(3), b =

12.972(3), c = 13.260(3) Å, α = 111.39(3), β = 100.95(3)°, γ = 114.32(3)°, V = 1724.0(12) Å^3, Z = 1, D_c = 2.632 gcm^{-3}, μ = 5.265 mm^{-1}, $F(000)$ = 1304, M = 2739.11, GOF = 1.054, data/parameters = 5900/458, $R_1[I > 2\sigma(I)]$ = 0.0654, wR_2 = 0.1848. The diffraction data were collected on a Rigaku Saturn70 CCD diffractometer in the range of 2.02–25.10° for **1** at 293 K with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). All absorption corrections were performed using the multiscan program. A total of 10486 reflections were collected, of which 5900 were unique. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97). All non-H atoms were located with successive difference Fourier syntheses and refined anisotropically. H atoms of dien ligands and coordinated water molecule were geometrically placed and refined using a riding model, while the H atoms of the free water molecules have not been included in the final refinement.

CCDC-730477 contains 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.

Supporting Information (see also the footnote on the first page of this article): TG curve, the plot of $\chi_M T$ vs. T, and χ_M^{-1} vs. T for **1**, as well as the projection of the 2-D network down the b axis of $[Co(en)_2][Co(bpy)_2]_2\ [PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot 4.5H_2O$.

Acknowledgments

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[1] a) J. T. Rhule, C. L. Hill, D. A. Judd, *Chem. Rev.* **1998**, *98*, 327–357; b) D. E. Katsoulis, *Chem. Rev.* **1998**, *98*, 359–387; c) M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48; d) A. Müller, H. Reuter, S. Dillinger, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2328–2361.

[2] a) M. I. Khan, E. Yohannes, R. J. Doedens, *Inorg. Chem.* **2003**, *42*, 3125–3129; b) M. I. Khan, L. M. Meyer, R. C. Haushalter, A. L. Schweitzer, J. Zubieta, J. L. Dye, *Chem. Mater.* **1996**, *8*, 43–53; c) B. Dong, J. Peng, C. J. Gómez-García, S. Benmansour, H. Jia, N. Hu, *Inorg. Chem.* **2007**, *46*, 5933–5941; d) M. I. Khan, E. Yohannes, R. J. Doedens, *Angew. Chem. Int. Ed.* **1999**, *38*, 1292–1294; e) Y. Lan, S. Li, X. Wang, K. Shao, D. Du, Z. Su, E. Wang, *Chem. Eur. J.* **2008**, *14*, 9999–10006; f) J.-W. Zhao, H.-P. Jia, J. Zhang, S.-T. Zheng, G.-Y. Yang, *Chem. Eur. J.* **2007**, *13*, 10030–10045.

[3] a) M. I. Khan, E. Yohannes, D. Powel, *Chem. Commun.* **1999**, 23–24; b) J. Do, R. P. Bontchev, A. J. Jacobson, *Inorg. Chem.* **2000**, *39*, 4305–4310; c) H. Tan, Y. Li, Z. Zhang, C. Qin, X. Wang, E. Wang, Z. Su, *J. Am. Chem. Soc.* **2007**, *129*, 10066–10067.

[4] S.-T. Zheng, J. Zhang, G.-Y. Yang, *Angew. Chem. Int. Ed.* **2008**, *47*, 3909–3913.

[5] a) C.-M. Liu, D.-Q. Zhang, M. Xiong, D.-B. Zhu, *Chem. Commun.* **2002**, 1416–1417; b) Y. Qi, Y. Li, C. Qin, E. Wang, H. Jin, D. Xiao, X. Wang, S. Chang, *Inorg. Chem.* **2007**, *46*, 3217–3230.

[6] a) A. Müller, J. Döring, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1721–1722; b) G. Han, M. A. Greaney, A. J. Jacobson, *J. Chem. Soc., Chem. Commun.* **1991**, 260–261; c) D. Gatteschi, B. Tsukerblat, A. L. Barra, L. C. Brunel, A. Müller, J. Döring, *Inorg. Chem.* **1993**, *32*, 2114–2117; d) R. Basler, G. Chaboussant, A. Sieber, H. Andres, M. Murrie, P. Kögerler, H. Bögge, D. C. Crans, E. Krickemeyer, S. Janssen, H. Mutka, A. Müller, H. U. Gudel, *Inorg. Chem.* **2002**, *41*, 5675–5685.

[7] Y. Qi, Y. Li, E. Wang, H. Jin, Z. Zhang, X. Wang, S. Chang, *Inorg. Chim. Acta* **2007**, 360,1841–1853.

[8] a) X.-B. Cui, J.-Q. Xu, Y. Li, Y.-H. Sun, G.-Y. Yang, *Eur. J. Inorg. Chem.* **2004**, 1051–1055; b) S.-T. Zheng, J. Zhang, J.-Q. Xu, G.-Y. Yang, *J. Solid State Chem.* **2005**, *178*, 3740–3746; c) S.-T. Zheng, Y.-M. Chen, J. Zhang, J.-Q. Xu, G.-Y. Yang, *Eur. J. Inorg. Chem.* **2006**, 397–406.

[9] a) X.-B. Cui, J.-Q. Xu, H. Meng, S.-T. Zheng, G.-Y. Yang, *Inorg. Chem.* **2004**, *43*, 8005–8009; b) S.-T. Zheng, J. Zhang, G.-Y. Yang, *Inorg. Chem.* **2005**, *44*, 2426–2430; c) S.-T. Zheng, M.-H. Wang, G.-Y. Yang, *Inorg. Chem.* **2007**, *46*, 9503–9508; d) Y. Qi, Y. Li, E. Wang, Z. Zhang, S. Chang, *Dalton Trans.* **2008**, 2335–2345.

[10] S.-T. Zheng, J. Zhang, B. Li, G.-Y. Yang, *Dalton Trans.* **2008**, 5584–5587.

[11] J. R. Fritch, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1978**, *100*, 3645–3646.

[12] I. D. Brown, D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.* **1985**, *41*, 244–247.

[13] G. Zhou, Y. Xu, C. Guo, X. Zheng, *Inorg. Chem. Commun.* **2007**, *10*, 849–852.

[14] a) X. Wang, J. Chen, J. Liu, *Cryst. Growth Des.* **2007**, *7*, 1227–1229; b) Q. Fang, G. Zhu, M. Xue, Z. Wang, J. Sun, S. Qiu, *Cryst. Growth Des.* **2008**, *8*, 319–329; c) A. Schaate, S. Klingelhöfer, P. Behrens, M. Wiebcke, *Cryst. Growth Des.* **2008**, *8*, 3200–3205; d) J.-W. Zhao, B. Li, S.-T. Zheng, G.-Y. Yang, *Cryst. Growth Des.* **2007**, *7*, 2658–2664.

[15] a) Q. Zhai, C. Lu, X. Wu, S. R. Batten, *Cryst. Growth Des.* **2007**, *7*, 2332–2342; b) Y. Yao, Y. Che, J. Zheng, *Inorg. Chem. Commun.* **2008**, *11*, 1253–1255; c) R. J. Hill, D.-L. Long, P. Hubberstey, M. Schröder, N. R. Champness, *J. Solid State Chem.* **2005**, *178*, 2414–2419.

[16] H. Sun, Z. Wang, S. Gao, *Inorg. Chem.* **2005**, *44*, 2169–2176.

[17] S.-T. Zheng, Y.-M. Chen, J. Zhang, G.-Y. Yang, *Z. Anorg. Allg. Chem.* **2006**, *632*, 155–159.

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