Inorg. Chem. **2003**, *42*, 7309–7314

Inorganic Chemistry
Article

Structure and Properties of a Novel 3D Straight-Channel Polyoxovanadate and an Unexpected Trimeric Barbiturate Obtained by Hydrothermal Reactions

Wenbin Yang, Canzhong Lu,* Quanzheng Zhang, Shumei Chen, Xiaoping Zhan, and Jiuhui Liu

The State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P.R.China

Received May 23, 2003

The hydrothermal reaction of $NaVO_3 \cdot H_2O$, barbituric acid, $NH_2NH_2 \cdot 2HCl$, H_3PO_4, and H_2O gave a novel heteropolyoxovanadate $Na_6[(P^VO_4)V^V_6V^{IV}_{12}O_{39}]_2 \cdot H_3PO_4 \cdot 31H_2O$ (**1**) and an unexpected phase $Na_2[C_{12}H_6N_6O_9] \cdot 7H_2O$ (**2**). The basic building blocks in **1** are the six-capped sphere-shaped heteropoly anion $[(P^VO_4)V^V_6V^{IV}_{12}O_{39}]^{3-}$ with framework similar to that of the reported polyoxovanadates possessing $\{V_{18}O_{42}\}$ clusters encapsulating VO_4 or other ions. These heterpoly anionic units are linked via V–O–V bridges into an interesting 3D straight-channel structure. The structure of **2** consists of novel organic anions ($[C_{12}H_6N_6O_9]^{2-}$, 5,5-bis(2′,4′,6′-trioxopyrimidyl)barbital, representing the first oxidized barbituric acid trimer) linked via sodium ions into 1D hollow tubes with diameter of 4.49 × 6.86 Å and further connected into a three-dimensional framework via hydrogen bonds.

Introduction

Owing to their unusual topological properties and economically important applications in many fields such as catalysis, biology, medicine, materials science, and magnetochemistry,[1] polyoxometalates have aroused particular interest for a long time.[2,3] However, it is still rather hard to design a multistep sequence for the synthesis of a given material with well-defined cavities and surface possessing different reactive sites or areas. Of the large polyoxometalate family, the most interesting subarea is polyoxovanadates, which are known to exhibit interesting physical and chemical properties with relevance to catalysis, biochemical processes, and materials science.[1,4] In contrast to the extensive research on discrete polyoxovanadates containing 4−34 vanadium atoms,[5] assembling of the well-characterized polyoxoanionic clusters to prepare desirable materials with well-defined pores in the crystal structures remains a great challenge. To date, the known examples are Khan's three-dimensional frameworks that consist of spherical $[V_{18}O_{42}(XO_4)$ clusters linked by bridging $[M(H_2O)_4]$ groups ($X = V, S$; $M = Fe, Co, Mn, Zn$).[6]

In this paper we present a novel polyoxovanadate $Na_6[(P^VO_4)V^V_6V^{IV}_{12}O_{39}]_2 \cdot H_3PO_4 \cdot 31H_2O$ (**1**), which is synthesized from the hydrothermal treatment of $NaVO_3 \cdot H_2O$, barbituric acid, $NH_2NH_2 \cdot 2HCl$, H_3PO_4, and H_2O. Interestingly, the above hydrothermal reaction yields another unexpected phase, $Na_2[C_{12}H_6N_6O_9] \cdot 7H_2O$ (**2**), a novel trimeric barbiturate sodium salt. Although the sphere-shaped building blocks in **1**, $[(P^VO_4)V^V_6V^{IV}_{12}O_{39}]^{3-}$, have a framework similar to that of the reported polyoxovanadates possessing $\{V_{18}O_{42}\}$ clusters encapsulating VO_4 or other ions,[7] these anionic units are linked via V−O−V bridges

---

* To whom correspondence should be addressed. E-mail: czlu@ms.fjirsm.ac.cn. Fax: 0086-0591-3714946.

(1) (a) Pope, M. T. *Heteropoly and Isopoly oxometalates*; Springer-Verlag: Berlin, 1983. (b) Pope, M. T.; Müller, A. *Polyoxometalates: From Platonic Solids to Anti-retroviral Activity*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994. (c) Zeng, H.; Newkome, G. R.; Hill, C. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1771.

(2) (a) A comprehensive review on polyoxometalates has been given by Hill et. al.: *Chem. Rev.* **1998**, *98*, 1−389. (b) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.

(3) (a) Zhang, S. W.; Wei, Y. G.; Yu, Q.; Shao, M. C.; Tang, T. Q. *J. Am. Chem. Soc.* **1997**, *119*, 6440. (b) Bösing, M.; Loose, I.; Phlmann, H.; Krebs, B. *Chem.*−*Eur. J.* **1997**, *3*, 1232.

(4) Karet, G. B.; Sun, Z.; Heinrich, D. D.; McCusker, J. K.; Folting, K.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1996**, *35*, 6450.

(5) Müller, A.; Reuter, H.; Dillinger, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2328.

(6) (a) Khan, M. I.; Yohames, E.; Powell, D. *Chem. Commun.* **1999**, *38*, 23. (b) Khan, M. I.; Yohames, E.; Doedens, R. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1292. (c) Khan, M. I.; Yohames, E.; Powell, D. *Inorg. Chem.* **1999**, *38*, 212.

(7) (a) Suber.; Bonamico, M.; Fares, V. *Inorg. Chem.* **1997**, *36*, 2030. (b) Müller, A.; Sessoli, R.; Krickemeyer, E.; Bögge, H.; Meyer, J.; Gatteschi, D.; Pardi, L.; Westphal, J.; Hovemeier, K.; Rohlfing, R.; Döring, J.; Hellweg, F.; Beugholt, C.; Schmidtmann, M. *Inorg. Chem.* **1997**, *36*, 5239.

10.1021/ic034554p CCC: $25.00

into an interesting 3D straight-channel structure, representing an example of 3D polyoxometalates based 100% on well-defined multicapped Keggin anionic units. The structure of **2** consists of the novel barbituric acid trimeric anions ($[C_{12}H_6N_6O_9]^{2-}$, 5,5-bis(2′,4′,6′-trioxopyrimidyl)barbital) linked via sodium ions into 1D hollow tubes with diameter of 4.49 × 6.86 Å and further connected into a three-dimensional framework via hydrogen bonds. The results of elemental analysis, NMR and IR spectra, and magnetic properties are also presented to support the structural determination.

Experimental Section

Reagents were purchased from Aldrich Chemical Co. and used without further purification. The elemental analyses of C, H, and N were performed on an Elementar Vario ELIII, and the contents of Na and V were determined by the atomic absorption method. All IR (KBr pellet) spectra were recorded using a Nicolet Magna 750FT-IR spectrometer. NMR spectra were measured on a Varian Unity-500 spectrometer (D_2O as solvent), operating at 125.704 and 202.329 MHz for ^{13}C and ^{31}P, respectively. Chemical shifts in D_2O solution were recorded using cyclohexane and H_3PO_4 as ^{13}C NMR and ^{31}P external reference standards. The magnetic susceptibility data for **1** were measured with a SQUID magnetometer in the range 5−300 K.

Synthesis of $Na_6[(PVO_4)V^V_6V^{IV}_{12}O_{39}]_2 \cdot H_3PO_4 \cdot 31H_2O$ (1) and $Na_2[C_{12}H_6N_6O_9] \cdot 7H_2O$ (2). The hydrothermal reaction was carried out in a 25 mL Teflon-lined stainless autoclave under autogenous pressure. A mixture of $NaVO_3 \cdot H_2O$ (0.237 g, 1.5 mmol), barbituric acid (0.492 g, 3.0 mmol), $NH_2NH_2 \cdot 2HCl$ (0.021 g, 0.3 mmol), H_3PO_4 (85wt %, 1.152 g, 10.0 mmol), and H_2O (14.5 mL) in a molar ratio of 1.5:3.0:0.3:10.0:800 was sealed in a 25 mL Teflon-lined stainless autoclave and heated to 180 °C for 2 days under autogenous pressure. After being slowly cooled to room temperature, the resultant dark colored solution was kept at room temperature in a narrow-necked Erlenmeyer flask for 10 days, resulting in black cubic crystals (about 40% yield based on V) of **1** and yellow needlelike crystals of **2** (about 55% based on barbituric acid). The two different kinds of crystals were isolated mechanically, washed with cooled water, and dried in air. Anal. Calcd for $H_{65}Na_6O_{121}P_3V_{36}$ (**1**): H, 1.61; V, 45.10; Na, 3.39; P, 2.29. Found: H, 1.59; V, 45.17; Na, 3.35; P, 2.27. IR (KBr pellet, ν (cm^{-1})): 3527 (s), 3444 (s), 3354 (s), 1622 (m), 1169 (s), 1088 (vs), 1036 (vs), 964 (vs), 901 (vs), 683 (m), 623 (m), and 553 (s). ^{31}P NMR (δ, H_3PO_4): 2.987 ppm. Anal. Calcd for $C_{12}H_{20}N_6Na_2O_{16}$ (**2**): H, 3.66; C, 26.17; N, 15.26; Na, 8.36. Found: H, 3.65; C, 26.14; N, 15.31; Na, 8.34. ^{13}C NMR (125 MHz) (δ, cyclohexane): 66.500, 88.519, 139.759, 155.078, 155.261, 167.084, and 176.480 ppm. IR (KBr pellet, ν (cm^{-1})): 3412 (s), 3157 (s), 2846 (s), 1693 (vs), 1578 (vs), 1458 (m), 1446 (m), 1414 (s), 1394 (s), 1367 (vs), 1348 (vs), 1238 (m), 1201 (m), 1169 (w), 1076 (w), 1055 (w), 1016 (w), 962 (w), 926 (w), 837 (m), 785 (m), 752 (m), 708 (m), 660 (m), 534 (s), 517 (m). Raman ($\lambda = 1064$ nm, KBr diluted, ν (cm^{-1})): 1733 (m), 1629 (m), 1446 (m), 626 (s), 458 (s).

X-ray Crystallography. A suitable crystal with dimensions of 0.31 × 0.31 × 0.31 for **1** and 0.4 × 0.18 × 0.1 mm^3 for **2** was carefully selected under a microscope and mounted on a glass fiber. Reflection data were collected on a Simens SMART CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at room temperature. In both cases, an empirical absorption correction by SADABS was applied to the intensity data. Structures were solved by direct methods and successive Fourier difference synthesis and refined by the full-matrix least-squares method on F^2 using the SHELXL-97 software. All non-hydrogen atoms were refined anisotropically. Partial H atoms in **1** and all the H atoms in **2** were located from the Fourier difference synthesis and introduced in the refinement as fixed isotropic contributors. Final structure solution and refinement gave R_1 (wR_2) = 0.0471 (0.1200) and $S = 1.068$ on the basis of 536 ($R_{int} = 0.0391$) reflections and 61 parameters for **1** and R_1 (wR_2) = 0.0714 (0.1824) and $S = 1.012$ for 3639 reflections ($R_{int} = 0.0334$) and 397 parameters for **2**.

Crystallographic data and other experimental details of the data collection for **1** and **2** are summarized in Table 1. Final atomic coordinates and thermal parameters of all non-hydrogen atoms, full bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and bond valence sum calculations are available in the tables of the Supporting Information. Selected bond lengths and angles of two compounds are given in Tables 2 and 3, respectively.

Results and Discussion

One-pot hydrothermal reactions are known to generate, sometimes, surprisingly new and unexpected phases.[8] Here, when we attempted the utilization of barbituric acid to the design synthesis of new inorganic−organic hybrid polyoxovanadates, an unexpected trimeric barbiturate sodium salt $Na_2[C_{12}H_6N_6O_9] \cdot 7H_2O$ (**2**) was produced together with the novel 3D straight-channel polyoxovanadate $Na_6[(P^VO_4)V^V_6V^{IV}_{12}O_{39}]_2 \cdot H_3PO_4 \cdot 31H_2O$ (**1**). The experimental results show that compound **1** can also be prepared in 30−55% yield from 160 to 195 °C without barbituric acid, suggesting that the role of barbituric acid in the synthesis of the polyoxovanadate cluster compound is not very important. However, the crystallization of **1** was found to be sensitive to the pH value of the starting mixture. The starting material of H_3PO_4 not only plays a reaction ligand role but also adjusts the pH value of the reaction mixture. In addition, the barbituric acid trimer **2** cannot be formed in the absence of $NaVO_3 \cdot H_2O$, indicating that $NaVO_3 \cdot H_2O$, maybe a hydrothermal reactive intermediate or product, plays an important role for the formation of **2**. The synthesis of barbiturates has been accomplished by a variety of conventional chemical methods, since they play economically important roles in pharmacy.[9] However, there is only one important route: barbiturates were generally synthesized by starting with the alkylation of a malonate, followed by reaction with a urea derivative.[10] Reported here is a very simple and single-step synthesis. The formation of the barbituric acid trimer may involve an oxidation of the enol and then radical coupling product (it is extremely difficult to provide another mechanism that couples these diketone-activated C−H bond positions).

The X-ray diffraction analysis reveals that the basic building block units in**1** are sphere-shaped $[(P^VO_4)V^V_6V^{IV}_{12}O_{39}]^{3-}$ (**1a**) clusters constructed from a $\{V_{18}O_{42}\}$[11] shell encapsulating a tetrahedral PO_4 group (Figure 1a). Two

---

(8) (a) Rao, C. N. R.; Natarajan, S.; Choudhury, A.; Neeraj, S.; Ayi, A. A. *Acc. Chem. Res.* **2001**, *34*, 80. (b) Cheetham, A. K.; Férey G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268.

(9) For some reviews, see: Bojarski, J. T.; Mokrosz, J. L.; Barton, H. J.; Paluchowska, M. H. *Adv. Heterocycl. Chem.* **1985**, *38*, 229.

(10) Qian, C. Y. *J. Org. Chem.* **1993**, *58*, 4448.

Table 1. Crystallographic Data and Structure Refinement Parameters for **1** and **2**

	1	**2**
formula	$H_{65}Na_6O_{121}P_3V_{36}$	$C_{12}H_{20}N_6Na_2O_{16}$
fw	4066.21	550.32
cryst system	cubic	triclinic
space group	$Fm\bar{3}m$	$P\bar{1}$
a (Å)	22.1978(15)	8.0888(5)
b (Å)	22.1978(15)	10.5501(7)
c (Å)	22.1978(15)	13.2798(9)
α (deg)	90	106.028(2)
β (deg)	90	103.547(2)
γ (deg)	90	93.244(2)
V (Å^3)	10937.8(13)	1049.95(12)
Z	4	2
D_{calc} (g cm^{-3})	2.469	1.741
μ (cm^{-1})	31.12	1.94
T	293(2)	293(2)
λ (Å)	0.710 73	0.710 73
θ range (deg)	$4.11 \le \theta \le 25.04$	$1.65 \le \theta \le 25.00$
h, k, l range	$-4 \le h \le 26$	$-9 \le h \le 7$
	$-14 \le k \le 20$	$-12 \le \text{h} \le 12$
	$-10 \le l \le 24$	$-15 \le h \le 15$
R [$I > 2\sigma(I)$]^a	R1 = 0.0471	R1 = 0.0714
	wR2 = 0.1200	wR2 = 0.1824
R (all data)	R1 = 0.0605	R1 = 0.1145
	wR2 = 0.1311	wR2 = 0.2205

^{a} $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR = \{\Sigma[(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**^{a}

V(1)−O(2)	1.617(5)	V(1)−V(2)	2.829(3)
V(1)−O(4)	1.9071(16)	V(1)−V(1)$^{\#2}$	3.3607(17)
V(1)−O(3)	1.912(2)	V(1)−V(1)$^{\#1}$	3.6580(18)
V(1)−O(1)	2.392(5)	V(2)−V(1)$^{\#3}$	2.829(3)
V(2)−O(5)	1.714(6)	V(2)−V(2)$^{\#4}$	3.428(13)
V(2)−O(4)	1.822(5)	O(2)−O(8)	2.951(8)
V(2)−O(3)	2.120(6)	O(2)−O(7)	3.170(4)
P(1)−O(1)	1.528(8)	O(4)−O(7)	3.002(8)
P(2)−O(9)	1.97(3)	O(6)−O(3)$^{\#5}$	2.760(8)
O(2)−V(1)−O(4)	100.5(2)	O(5)−V(2)−O(4)	116.6(2)
O(2)−V(1)−O(3)	99.60(18)	O(5)−V(2)−O(3)	102.9(2)
O(4)−V(1)−O(3)	88.0(2)	O(1)$^{\#6}$−P(1)−O(1)	109.471(1)
O(2)−V(1)−O(1)	170.5(2)	O(9)$^{\#7}$−P(2)−O(9)	83.6(3)
O(4)−V(1)−O(1)	86.34(18)	P(1)−O(1)−V(1)	125.78(15)
O(3)−V(1)−O(1)	73.79(16)	V(1)$^{\#2}$−O(1)−V(1)	89.3(2)

Symmetry transformations used to generate equivalent atoms: #1, $z, -x, -y$; #2, $-z - 1/2, x + 1/2, -y$; #3, $y - 1/2, -z, -x - 1/2$; #4, $-x - 1/2, -y, -z - 1/2$; #5, $x, -y, z$; #6, $-x - 1/2, -y + 1/2, z$; #7, $z - 1/2, x + 1/2, -y$.

unique vanadium sites exhibit different coordination environments: V(1) is octahedrally bonded to a terminal oxo group (V(1)═O(2), 1.617(5) Å), four μ_3-oxygens of the shell (two V(1)−O(3), 1.912(2) Å, and two V(1)−O(4), 1.9071(16) Å), and one μ_4-O from the central PO_4 group (V(1)−O(1), 2.392(5) Å), whereas V(2) resides in a square-pyramidal geometry defined by four basal oxygen (V(2)−O(3), 2.120(6) Å, and two V(2)−O(4), 1.822(5) Å) and an apical μ_2-oxygen (V2)−O(5), 1.714(6) Å), which in turn is linearly bonded to another V(2) center of the neighboring $[(P^{V}O_4)V^{V}{}_6V^{IV}{}_{12}O_{39}]^{3-}$ unit.

Alternatively, the structure of **1a** can be considered as based on the well-known Keggin fragment $\{(PO_4)V_{12}O_{36}\}$, in which four basic trinuclear units $\{V_3O_{13}\}$ share corners with a central PO_4 tetrahedron and then six terminal VO^{2+} units are capped to the six equivalent (100) square windows formed by 24 oxygen atoms, generating a six-capped Keggin ion. An important structural feature of **1** is that each square-pyramidal vanadium atom forms four V−V pairs with short V−V distances of 2.829(3) Å, resulting in a "metal" sphere. The V−V distances are comparable with the values for most known mixed-valence polyoxovanadates.[12] Although a series

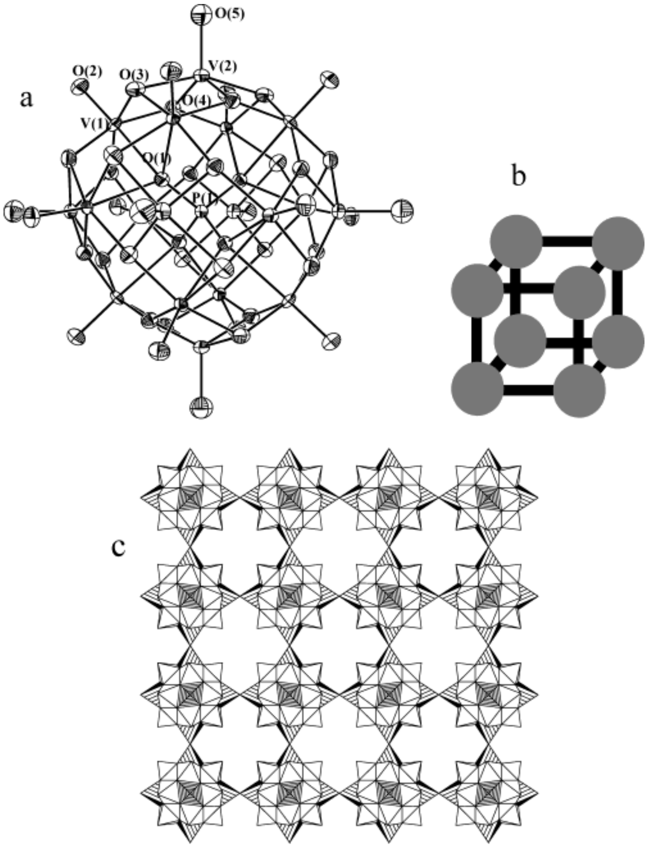

Figure 1. (a) Ortep drawing of the six-capped Keggin type building block in **1** with the atom labeling scheme for the asymmetric unit. (b) Schematic representation of the cubic cage in **1** with a cluster anion at each corner. (c) 3D rectangular channels formed by $\{V_{18}O_{42}(PO_4)\}$ blocks via V−O−V bridges (viewed along *a*, *b*, or *c* axis; polyhedra in parent Keggin moieties, blank; capping VO_5 square pyramids, parallel lines).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Na(1)−O(7)	2.247(3)	O(3)−C(4)	1.216(5)	C(3)−N(2)	1.364(6)
Na(1)−O(1)	2.336(4)	O(4)−C(6)	1.257(5)	C(4)−N(2)	1.364(6)
Na(1)−O(11)	2.348(5)	O(5)−C(7)	1.314(2)	C(5)−C(6)	1.412(6)
Na(1)−O(12)	2.374(4)	O(6)−C(8)	1.246(5)	C(6)−N(3)	1.388(6)
Na(2)−O(13)	2.308(5)	O(7)−C(10)	1.245(5)	C(7)−N(4)	1.325(5)
Na(2)−O(14)	2.341(5)	O(8)−C(11)	1.315(2)	C(8)−N(4)	1.411(6)
Na(2)−O(12)	2.429(6)	O(9)−C(12)	1.268(5)	C(9)−C(12)	1.395(6)
Na(2)−O(11)	2.666(6)	C(1)−C(5)	1.530(6)	C(10)−N(5)	1.402(6)
O(1)−C(2)	1.223(5)	C(1)−C(4)	1.538(6)	C(11)−N(6)	1.319(6)
O(2)−C(3)	1.223(5)	C(2)−N(1)	1.375(5)	C(12)−N(6)	1.319(6)

O(7)−Na(1)−O(1)	90.60(12)	C(6)−C(5)−C(8)	118.9(4)
O(1)−Na(1)−O(11)	92.32(16)	O(4)−C(6)−N(3)	117.8(4)
O(11)−Na(1)−O(12)	90.54(17)	N(4)−C(7)−N(3)	119.8(3)
O(13)−Na(2)−O(14)	95.56(18)	N(4)−C(8)−C(5)	116.0(4)
O(14)−Na(2)−O(12)	123.6(2)	C(12)−C(9)−C(10)	118.9(4)
O(13)−Na(2)−O(11)	81.15(17)	O(7)−C(10)−C(9)	128.8(4)
C(5)−C(1)−C(9)	115.1(3)	N(6)−C(11)−N(5)	119.0(3)
C(9)−C(1)−C(2)	105.8(3)	N(6)−C(12)−C(9)	118.9(4)
C(9)−C(1)−C(4)	109.8(3)	C(3)−N(1)−C(2)	124.5(4)
O(1)−C(2)−N(1)	118.9(4)	C(3)−N(2)−C(4)	125.6(4)
N(1)−C(2)−C(1)	118.6(4)	C(7)−N(3)−C(6)	122.3(3)
N(2)−C(3)−N(1)	117.4(4)	C(7)−N(4)−C(8)	123.3(3)
N(2)−C(4)−C(1)	118.4(4)	C(11)−N(5)−C(10)	124.3(4)

---

(11) Müller, A.; Penk, M.; Rohlfing, R.; Krickemeyer, E.; Döring, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 926.

of mono-, bi-, tetra-, and even six-capped Keggin derivatives have been synthesized from hydrothermal reactions,[13] few extended structures built up by capped Keggin ions have been reported.[6,14] Compound **1** represents an interesting example of three-dimensional network based 100% on well-defined multicapped Keggin anionic units. In **1**, each six-capped Keggin anion is connected to six other neighboring units via V(2)−O(5)−V(2) bridges (V(2)···V(2), 3.428(13) Å, and V(2)−O(5)−V(2), 180°). Such linkage manner leads to the formation of cubic cages with a cluster anion at each corner (Figure 1b), which were further arranged along three mutually perpendicular directions to generate 3D rectangular channels occupied by water and phosphate (H_3PO_4) molecules and sodium ions (Figure 1c).

Two crystallographically independent phosphate moieties have been revealed unambiguously from the Fourier difference synthesis. One is the type of PO_4^{3-}, and the other is the lattice H_3PO_4 molecule. However, the ^{31}P NMR spectrum only reveals a single resonance at $\delta = 2.987$ ppm. P(1) is just located in the center of the sphere-shaped $[(P^VO_4)V^V_6V^{IV}_{12}O_{39}]^{3-}$ cluster, and adopts typical tetrahedral geometry with P−O distances of 1.528(8) Å and O−P−O angles of 109.5°. P(2) lies at (−0.5, 0, 0), whereas the four O atoms bonded to P(2) are statistically located on 24 general positions each with occupancy of 1/6. The P(2)−O distances (1.97(3) Å), notably longer than those in previous PO_4 tetrahedra,[15] are close to the sum of P−O covalent radii (1.83 Å[16]) and can be comparable with the $O-P^V$ distances in many hypercoordination cyclic oxyphosphoranes and phosphates.[17−18] Another interesting feature of **1** is that the water of crystallization in the channels is not bonded to sodium ions and only hydrogen-bonded to oxygen atom of the polyoxometalate network (O···O, 2.76−3.17 Å). However, these water molecules and sodium ions constitute a large $[Na_6(OH_2)_{19}]^{6+}$ "group" with long $Na\cdots OH_2$ contacts of 3.176−3.257 Å, of which the framework is very similar to that of the Lindqvist-type[2a] polyoxoanions $[M_6O_{19}]^{n-}$. Lattice H_3PO_4 molecules and $[Na_6(OH_2)_{19}]^{6+}$ "groups" are alternately located in the above-mentioned cubic cage. The channel water molecules are easily dehydrated by the evacuation at 100 °C. An X-ray powder pattern of the dehydrated sample exhibits several sharp peaks and is in good agreement with a simulation of the single-crystal structure (see Supporting Information), showing no apparent skeletal changes in the structure after evacuation treatments.

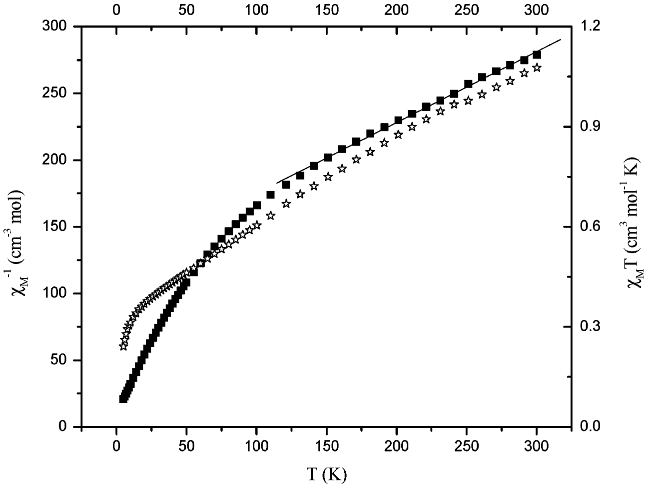

Figure 2. Temperature dependence of χ_M^{-1} and $\chi_M T$ for **1**.

To determine the electronic structure and the number of V^{IV} centers, compound **1** was further characterized by elemental analyses, redox titration, bond valence sums, and magnetic susceptibility. In the IR spectrum (KBr pellet) of **1**, a vibration at 964 cm^{-1} is assigned to the terminal V═O stretch [ν(V═O)] and bonds at 901, 683, 623, and 553 s cm^{-1} are characteristic of V−O−M [ν(V−O−M), M = V, P]. The V═O stretches are relatively low, and one may assume the involvement of the oxovanadium moieties in $V{=}O\cdots H_2O$ interactions confirmed by the short $V(1){=}O(2)\cdots O(8)H_2$ contact of 2.951(8) Å. Bands at 1169, 1088, and 1036 cm^{-1} are assigned to ν(P−O) of the phosphate. The vibrations at 3527, 3444, 3354, and 1622 cm^{-1} are associated with ν(O−H) or δ(H_2O). The black coloration of the crystals indicates that V atoms in **1** are in mixed-valence oxide states. Bond valence sum calculations[19] on the V coordination spheres give a value of 4.611 for V(1) and 3.818 for V(2), respectively. The average oxidation state is 4.347 (expected value for $V^V_6V^{IV}_{12}$ is 4.333), suggesting that the 3d^1 electrons in **1** are delocalized. The number of V^{IV} is supported by the result of redox titration of V^{IV} sites (12 ± 1 V^{IV}/building unit).

The magnetic behavior of **1** is shown in Figure 2 as χ_M^{-1} and $\chi_M T$ versus T plots. At $T = 300$ K, the $\chi_M T$ value, 1.077 emu K mol^{-1}, is much lower than the spin-only value for the 12 V^{IV} centers (4.5 emu K mol^{-1}) per formula, suggesting the presence of the very strong antiferromagnetic interactions between vanadium centers. The strong antifrromagnetism is also apparent from the fact that $\chi_M T$ plots decrease dramatically upon cooling and confirmed by the large negative Weiss constant (the magnetic susceptibility data of **1** in the high-temperature region from 120 to 300 K obey the Curie−Weiss Law $\chi = C_M/(T - \Theta)$ with $C_M = 1.88$ emu K mol^{-1} and Θ

---

(12) Müller, A.; Meyer, J.; Bögge, H.; Stammler, A.; Botar, A. *Chem.—Eur. J.* **1998**, *4*, 1388.

(13) (a) Zhang, Y.; Haushalter, R. C.; Clearfield, A. *Chem. Commun.* **1995**, 1149. (b) Xu, Y.; Zhu, H. G.; Cai, H.; You, X. Z. *Chem. Commun.* **1999**, 787. (c) Hill, L.; Prosser-McCartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407. (d) Hou, D.; Hagen, S. K.; Hill, C. L. *Chem. Commun.* **1993**, 426. (e) Xu, Y.; Zhu, D. R.; Guo, Z. J.; Shi, Y. J.; Zhang, K. L.; You, X. Z. *J. Chem. Soc., Dalton. Trans.* **2001**, 772. (f) Seling, A.; Anderson, I.; Petterssin, L.; Schramm, C. M.; Donwney, S. L.; Grate, J. H. *Inorg. Chem.* **1994**, *33*, 3141.

(14) Müller, A.; Koop, M.; Schiffels, P.; Bogge, H. *Chem. Commun.* **1997**, 1715.

(15) (a) Haushalter, R. C.; Lii, K. H.; O'Connor, C. M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 549. (b) Peloux, C. D.; Dolbecq, A.; Mialane, P.; Marrot, J.; Rivière, E.; Sécheresse, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 2455. (c) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 610.

(16) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(17) (a) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927. (b) Prakasha, T.; Day, K. R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 2690. (c) Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 6329.

(18) (a) Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 3747. (b) Wang, C. Y.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **1996**, *35*, 325. (c) Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1997**, *117*, 1317.

(19) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

$= -229.5$ K). Unfortunately, it is too difficult to fit the experimental magnetic data of this three-dimensional mixed-valence spin system using a suitable theoretical mode. A common feature of the class of mixed-valence polyoxovanadate structures possessing $\{V_{18}O_{42}\}$ clusters encapsulating VO_4 or other ions (e.g. NO_2^-, Br^-, Cl^-, and I^-) is the presence of strong antiferromagnetic coupling interactions that can be attributed to the electron delocalization on the 18 vanadium sites.[7] The same mechanism might operate in the present system. There are 48 connections between the 18 vanadium centers of a $[(P^{V}O_4)V^{V}_6V^{IV}_{12}O_{42}]^{3-}$ cluster unit (see Figure 7S in the Supporting Information), of which 24 involve single μ_3-O bridges (dashed lines) with a V−V average distance of 3.509 Å and the other 24 involve double μ_3-O bridges (solid lines) with V−V distances of 2.829(3) Å. These V−V distances have been considered in the literature as acceptable values for charge delocalization among vanadium centers.[7] In addition, the V(2)−V(2′) contacts (3.428(13) Å) between two neighboring cluster units, which involve a single μ_2-O bridge, are another important pathway to delocalize electrons and therefore to mediate antiferromagnetic interactions.

X-ray single-crystal diffraction analysis shows that the anion in **2**, 5,5-bis(2′,4′,6′-trioxopyrimidyl)barbital ($[C_{12}H_6N_6O_9]^{2-}$, **2a**), represents a novel trimeric form of barbituric acid. The structure of **2a** significantly differs from that of the reported trimeric cyclic barbiturate prepared via electrochemical oxidation of 1,3-dimethylbarbituric acid.[20] As shown in the stereoscopic view of **2a** (Figure 3a), two of the three barbiturate rings are covalently linked to the third one, forming normal C−C single bonds: C(1)−C(5) and C(1)−C(9), 1.530(6) Å. Each barbiturate ring is nearly planar, but rings B and C are twisted toward each other (B−C dihedral angle, 41.6°) and situated at either side of the ring A. The C−C distances in rings B and C vary between 1.395 and 1.421 Å, and only the C(1)−C(2) and C(1)−C(4) bonds in ring A are somewhat lengthened (average 1.534 Å). The C(7)−O(5) and C(11)−O(8) distances ($\approx$1.315 Å) are notably longer than other C−O distances (1.216−1.268 Å), and the corresponding C(5)−N and C(11)−N bonds are shorten (1.319−1.330 Å) in contrast to other C−N bonds (1.364−1.411 Å). These facts show that C(7)−O and C(11)−O bonds are normal single bonds and conjugated to C−N, whereas all other C−O bonds remain as C−O, forming a organic divalent anion $[C_{12}H_4N_6O_9]^{2-}$, which is chargedly balanced by two sodium ions.

Interestingly, the organic anions are linked via the $\{Na_2\}$ clusters into 1D hollow tubes with diameter of 4.49 × 6.86 Å (Figure 3c), where each $\{Na_2\}$ cluster is composed of two face-sharing polyhedra (Na−Na contact, 3.269 Å), namely, the $Na(1)O_4(OH_2)$ octahedron (Na(1)−O, 2.247−2.641, Na(1)−OH_2, 2.348−2.374 Å) and the $Na(2)O(OH_2)_4$ square pyramid (Na(2)−O, 2.286, Na(2)−OH_2, 2.308−2.666 Å). All the protons of the organic anions and water molecules have been located from Fourier different synthesis. There are some moderately strong N−H⋯O contacts (d(H⋯O) = 1.82−1.96 Å, d(N⋯O) = 2.783−2.919 Å, ∠(N−H⋯O) = 165−168°; Table 4), which involve the nitrogen atoms of a organic anion as hydrogen donors while the oxygen atoms of the neighboring organic anions act as acceptors. One of the organic nitrogens (N(6)) is also hydrogen bonded to a lattice water molecular. The corresponding geometrical parameters are of H(6)⋯O(16)$^{\#1}$, 1.92(2) Å, N(1)⋯O(16)$^{\#1}$, 2.877(5) Å, and ∠N(6)−H(6)⋯O16$^{\#1}$, 169(5)°. In addition, almost all hydrogen atoms of coordinated and lattice water molecules are involved in moderately strong hydrogen bonds

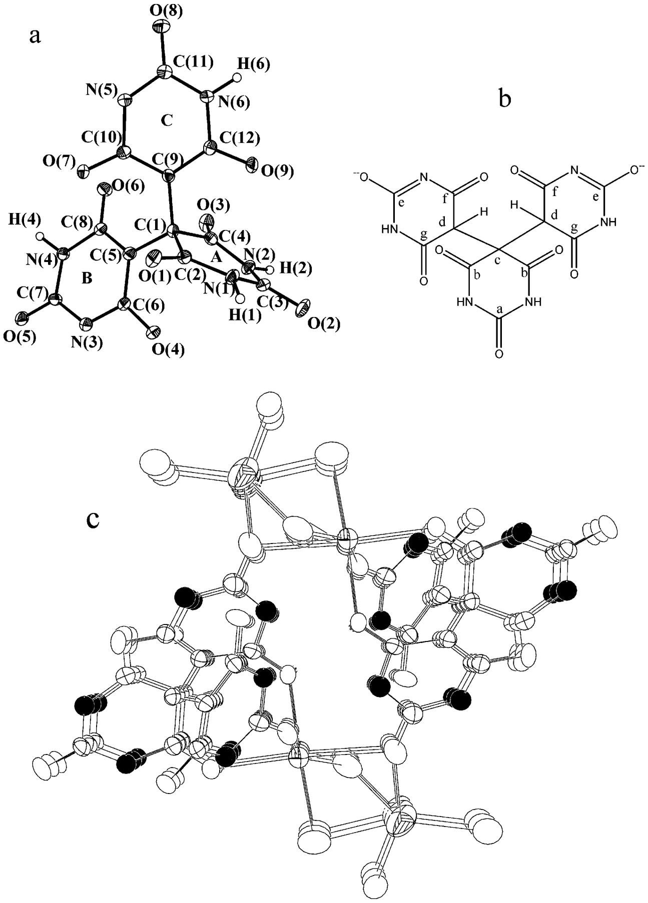

Figure 3. (a, b) Structure of the $[C_{12}H_6N_6O_9]^{2-}$ anion. (c) Hollow tubes (viewed along the *a* axis) formed by organic anion and Na^+ cations (Na, cross-hatched oval, O, open oval, N, solid circle, and C, crossed oval).

Table 4. Hydrogen-Bonding System for **2** (Å, deg)[a]

D−H⋯A	d(D−H)	d(H⋯A)	d(D⋯A)	∠(DHA)
N(1)−H(1)⋯O(4)$^{\#5}$	0.98(2)	1.82(2)	2.783(5)	165(4)
N(2)−H(2)⋯O(9)$^{\#10}$	0.97(2)	1.88(2)	2.837(5)	168(6)
N(4)−H(4)⋯O(7)$^{\#6}$	0.97(2)	1.96(2)	2.919(4)	167(5)
N(6)−H(6)⋯O(16)$^{\#1}$	0.97(2)	1.92(2)	2.877(5)	169(5)
O(11)−H(11A)⋯O(15)$^{\#1}$	1.01(5)	1.99(5)	2.959(7)	162(6)
O(11)−H(11B)⋯O(2)$^{\#5}$	1.04(5)	1.77(6)	2.778(6)	162(6)
O(12)−H(12A)⋯O(6)$^{\#6}$	0.98(5)	1.85(5)	2.834(5)	176(8)
O(12)−H(12B)⋯O(14)$^{\#7}$	0.97(5)	1.90(5)	2.858(6)	169(8)
O(13)−H(13A)⋯O(2)$^{\#5}$	1.02(5)	2.09(6)	2.993(5)	146(6)
O(13)−H(13B)⋯O(6)$^{\#8}$	0.96(5)	1.86(5)	2.806(5)	170(7)
O(15)−H(15A)⋯O(17)$^{\#5}$	0.92(5)	2.03(7)	2.837(6)	146(8)
O(16)−H(16A)⋯O(3)	1.06(6)	1.93(8)	2.793(5)	136(8)
O(17)−H(17A)⋯O(9)	0.95(5)	1.82(5)	2.763(5)	173(6)

[a] Symmetry transformations used to generate equivalent atoms: #1, $x - 1, y, z$; #2, $-x + 1, -y, -z + 1$; #3, $-x + 1, -y - 1, -z + 1$; #4, $x + 1, y, z$; #5, $-x + 2, -y, -z + 2$; #6, $-x + 2, -y, -z + 1$; #7, $-x + 2, -y - 1, -z + 1$; #8, $x, y - 1, z$; #9, $-x + 3, -y, -z + 2$.

---

(20) Kato, S.; Polling, M.; Herm, D.; Dryhurst, G. *J. Am. Chem. Soc.* **1974**, *96*, 5255.

(d(H$\cdots$O) = 1.77−2.09 Å, d(O$\cdots$O) = 2.763−2.993 Å, and ∠O−H$\cdots$O = 136−176°), where the oxygen acceptors either arise from the neighboring organic anions or from water molecules. Therefore, the above-mentioned tubes are further connected into a complicated three-dimensional network via hydrogen-bonding interactions.

The structure, as determined (Figure 3), is compatible with the spectra data. The IR spectrum of **2** exhibits four vibration regions: from 3412 (s) to 2846 (s) cm^{-1}, from 1693 (vs) to 1348 (vs) cm^{-1}, from 1238 (m) to 925 (w) cm^{-1}, and from 837 (m) to 501 (m) cm^{-1}. In the first region, the band at 3412 cm^{-1} is due to ν(O−H_2), 3157 and 3018 cm^{-1} are due to ν(N−H), and 2846 cm^{-1} is to ν(C−H). In the secondary region, the vibration at 1693 cm^{-1} is assigned to ν(C=O), while bands from 1578 to 1348 cm^{-1} are the skeleton vibrations of the heterocycles. The weak or moderate strong bands from 1238 to 926 cm^{-1} are assigned to ν(C−C), ν(C−O), or ν(C−N), and moderate strong bands within the 837−660 cm^{-1} range are the γ(C−H) vibrations. The ^{13}C NMR spectrum shows a complicated series of signals corresponding to the trimeric barbiturate ligands (ppm): 66.5 to Cd; 88.519 to Cc; 139.759 to Ce.

Conclusions

In this paper, we have structurally characterized a novel polyoxovanadate and an unexpected trimeric barbiturate, both obtained from the hydrothermal reaction of $NaVO_3 \cdot H_2O$, barbituric acid, $NH_2NH_2 \cdot 2HCl$, H_3PO_4, and H_2O. The successful syntheses of **1** and **2** prove again the advantages of hydrothermal techniques in designing new kinds of structural inorganic and organic solids. As for **1**, it has three interesting structural features: (1) the presence of six-capped Keggin polyoxometalate units with each capping vanadium atom forming four short V−V pairs to give a “metal” sphere; (2) the formation of 3D straight-channel framework via V−O−V bridges; (3) the presence of naked Na^+ ions which are coordinated neither to the lattice H_3PO_4 and H_2O molecules in the channels nor to the oxygens of the POM framework. It is also noted that compound **1** exhibit very strong antiferromagnetic coupling interactions attributed to the delocalization of $3d^1$ electrons on the whole 3D framework. The novel organic anions ($[C_{12}H_6N_6O_9]^{2-}$) in **2** represent the first oxidized barbituric acid trimer, which is linked via Na^+ ions into 1D hollow tubes and then further connected into a three-dimensional framework via hydrogen bonds.

Acknowledgment. The authors thank the 973 program of the MOST (Greant 001CB108906), the Natural Science Foundation of China (Grants 90206040, 20073048), the NSF of Fujian (Grants 2002F015, 2002J006), and the State Key Laboratory of Structural Chemistry (Grant 030065) for financial support.

Supporting Information Available: Tables of crystal data and refinement, atomic coordinates, thermal parameters, bond distances, and bond angles (also in CIF format), BVS calculations, a powder X-ray diffraction pattern, IR spectra, and ^{13}C NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC034554P