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# A layered vanadium arsenate network decorated with the directly coordinated organonitrogen ligands: $[V_4O_7(HAsO_4)_2(o\text{-phen})_2]$ (*o*-phen = *o*-phenanthroline)

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## Abstract

A novel layered vanadium arsenate  $[V_4O_7(HAsO_4)_2(o\text{-phen})_2]$  **1** (*o*-phen = *o*-phenanthroline) was synthesized by the hydrothermal reaction of  $V_2O_5$ ,  $ZnCl_2$ ,  $Na_2HAsO_4 \cdot 7H_2O$ , *o*-phenanthroline (*o*-phen) and water. Its structure was determined by elemental analyses, ESR spectrum, XPS spectrum, TG analysis, IR spectrum and the single-crystal X-ray diffraction. Compound **1** crystallizes in monoclinic system, space group  $P2/c$ ,  $a = 10.122(2)$  Å,  $b = 9.867(2)$  Å,  $c = 15.367(3)$  Å,  $\beta = 102.83(3)^\circ$ ,  $V = 1496.4(5)$  Å<sup>3</sup>,  $Z = 1$ ,  $\lambda(\text{MoK}\alpha) = 0.71073$  Å, ( $R(F) = 0.0397$  for 3422 reflections). Data were collected on a Rigaku R-AXIS RAPID IP diffractometer at 293 K in the range of  $2.06^\circ < \theta < 27.48^\circ$ . The title compound contains an unusual two-dimensional (2D) As–V–O layer with four-, six- and eight-membered rings. The chelating *o*-phen ligands project perpendicularly above and below the undulating layer. **1** represents the first example of 2D inorganic vanadium arsenate backbone grafted with the directly coordinated organic ligands. Furthermore, the 3D supermolecular architecture is formed by  $\pi$ – $\pi$  stacking interactions of the *o*-phen groups between adjacent layers.

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**Keywords:** Organic–inorganic hybrid; Layered vanadium arsenate; Hydrothermal synthesis; Directly coordinated organic ligands

## 1. Introduction

Polyoxovanadates have been attracting extensive interest in solid state materials chemistry owing to their interesting structural features and various potential applications in catalysis, electron conductivity, magnetism and photochemistry [1–4]. In this field, an important advance recently is the modification of inorganic vanadium oxides with various organic ligands and transition metal complexes or fragments. Based on this strategy, a large number of new compounds have been synthesized and structurally characterized in the V–P–O system [5–10]. They exhibit varieties of novel frameworks and have potential applications in catalysis and

materials science [11, 12]. In contrast to abundant compounds in the {V/P/O} system, the {V/As/O} system remains relatively undeveloped. In the past years, reports have been concentrated on the discrete vanadium arsenate clusters [13–15], for example, the  $K_6[As_6V_{15}O_{42}(H_2O)] \cdot 8H_2O$  [13] and anionic porous skeletons such as  $MVOAsO_4$  ( $M = Na, Li, NH_4$ ) [16] and  $[Cs_3(VO)_2(V_2O_3)(AsO_4)(HAsO_4)_2]$  [17]. Recently, the introduction of hydrothermal technique and the use of organic templating agents have led to the production of some vanadium arsenate phases with two-dimensional (2D) layer-like and 3D porous structures, such as  $[H_2NC_4H_8NH_2][(VO)_2(HAsO_4)_2(H_2AsO_4)_2]$  [18] and  $[AsV_8^{IV}V_2^{V}O_{26}(H_2O)] \cdot 8H_2O$  [19], in which the organic templates act as counter cations or structural filling agents. To the best of our knowledge, vanadium arsenate complexes containing organic components functioning as ligands coordinated directly to the vanadium arsenate backbone or to the secondary metal

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centers are rare. Since vanadium-oxide-phosphates system exhibits extensive coordination chemistry with the organic ligands, the solids constructed from {V/As/O} system may also have the feasibility for the incorporation of appropriate organic ligand moieties. This offers opportunities for preparing novel organic–inorganic hybrid materials containing inorganic {V/As/O} scaffoldings decorated with organic ligand functional units.

In this work we report on the hydrothermal synthesis and crystal structure of a novel organic–inorganic hybrid vanadium arsenate,  $[V_4O_7(HAsO_4)_2(o\text{-phen})_2]$  **1** (*o*-phen = *o*-phenanthroline). Compound **1** contains an unusual 2D {V/As/O} skeleton with the *o*-phen fragments coordinated directly to the inorganic layer. To the best of our knowledge, **1** represents the first example of 2D inorganic vanadium arsenate backbone decorated with the directly coordinated organic ligands.

## 2. Experimental section

### 2.1. General procedures

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. V and As were determined by a Leaman inductively coupled plasma spectrometer. ESR spectrum was recorded on a Japanese JES-FE3AX spectrometer at 293 K. XPS analysis was performed on a VG ESCALABMK II spectrometer with an MgK $\alpha$  (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at  $6.2 \times 10^{-6}$  Pa during the analysis. IR spectrum was recorded in the range 400–4000  $\text{cm}^{-1}$  on an Alpha Centaur FT/IR spectrophotometer using KBr pellets. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing  $N_2$  with a heating rate of  $10^\circ\text{C min}^{-1}$ .

### 2.2. Hydrothermal synthesis

A mixture of  $V_2O_5$  (0.192 g),  $ZnCl_2$  (0.068 g),  $Na_2HAsO_4 \cdot 7H_2O$  (0.186 g), *o*-phen (0.198 g) and  $H_2O$  (9 mL) was stirred for 1 h in air. The mixture was sealed in a 20 mL Teflon-lined autoclave and heated at  $170^\circ\text{C}$  for 144 h. Then the autoclave was cooled at  $10^\circ\text{C h}^{-1}$  to room temperature. The resulting black block crystals **1** were filtered off, washed with distilled water, and dried at ambient temperature (yield 50% based on vanadium).  $ZnCl_2$  is necessary for this reaction though zinc is not incorporated into the structure of compound **1**. The black crystals were manually selected for structural determination and further characterization. The elemental analyses found: C, 30.05; H, 1.98; N, 5.90; As, 15.73; V, 21.23%; Calc. for  $C_{24}H_{18}As_2N_4O_{15}V_4$ : C,

30.15; H, 1.90; N, 5.86; As, 15.67; V, 21.31%. IR spectrum ( $\text{cm}^{-1}$ ): 3430, 1627, 1518, 1423, 1139, 1106, 1051, 981, 927, 912, 869, 773, 724, 678, 647, 517.

### 2.3. X-ray crystallography

The structure of compound **1** was determined by single crystal X-ray diffraction. Crystallographic data are as follows:  $C_{24}H_{18}As_2N_4O_{15}V_4$ , monoclinic,  $P2_1/c$ ,  $a = 10.122(2)$  Å,  $b = 9.867(2)$  Å,  $c = 15.367(3)$  Å,  $\beta = 102.83(3)^\circ$ ,  $V = 1496.4(5)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_{\text{cal}} = 1.079$ ,  $\lambda$  (MoK $\alpha$ ) = 0.71073 Å. A black single crystal of **1** ( $0.678 \times 0.544 \times 0.342$  mm<sup>3</sup>) was mounted inside a glass fiber capillary. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer. Empirical absorption correction ( $\psi$  scan) was applied. The structure was solved by the direct method and refined by the Full-matrix least squares on  $F^2$  using the SHELXTL-97 software [20]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atom attached to oxygen atom was located in its calculated position and those attached to carbon atoms were located from difference Fourier maps. A total of 6499 (3422 unique,  $R_{\text{int}} = 0.0376$ ) reflections were measured. Structure solution and refinement based on 3422 independent reflections with  $I > 2\sigma(I)$  and 222 parameters gave  $R_1(wR_2) = 0.0397$  (0.1300)  $\{R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}\}$ . A summary of crystal data and structure refinement for compound **1** is provided in Table 1. The selected bond lengths and angles are listed in Table 2. The atomic coordinates and equivalent isotropic displacement parameters for **1** are given in Table 3.

CCDC reference number 197034.

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

Empirical formula	$C_{24}H_{18}As_2N_4O_{15}V_4$
Formula weight	956.02
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 10.122(2)$ Å, $\alpha = 90^\circ$ $b = 9.867(2)$ Å, $\beta = 102.83(3)^\circ$ $c = 15.367(3)$ Å, $\gamma = 90^\circ$
Volume	$1496.4(5)$ Å <sup>3</sup>
$Z$	2
$D_c$	$2.122$ mg/m <sup>3</sup>
Absorption coefficient	$3.487$ mm <sup>-1</sup>
$\theta$ range for data collection	$2.06$ – $27.48^\circ$
Reflections collected	6499
Independent reflections	$3422 [R_{\text{int}} = 0.0376]$
Max. and min. transmission	0.550 and 0.295
Data/restraints/parameters	3422/0/222
Final $R$ indices $[I > 2\sigma(I)]$	$R_1 = 0.0397$ , $wR_2 = 0.1300$
$R$ indices (all data)	$R_1 = 0.0593$ , $wR_2 = 0.1688$

Table 2  
Selected bond lengths (Å) and angles (deg) for **1**

V(1)–O(7)	1.603(4)	V(1)–O(6)	1.663(3)
V(1)–O(1)#2	1.834(4)	V(1)–O(8)	1.7768(10)
V(2)–O(3)	1.999(3)	V(2)–O(5)	1.588(3)
V(2)–N(2)	2.129(4)	V(2)–O(4)#1	1.965(3)
V(2)–N(1)	2.306(4)	V(2)–O(6)	1.985(3)
As(1)–O(1)	1.710(4)	As(1)–O(2)	1.698(3)
As(1)–O(3)	1.653(3)	As(1)–O(4)	1.671(3)
O(5)–V(2)–O(4)#1	104.62(18)	O(4)#1–V(2)–N(1)	88.76(14)
O(5)–V(2)–O(6)	96.37(16)	O(6)–V(2)–N(1)	85.34(14)
O(4)#1–V(2)–O(6)	84.65(14)	O(3)–V(2)–N(1)	79.20(13)
O(5)–V(2)–O(3)	99.25(15)	N(2)–V(2)–N(1)	74.03(14)
O(4)#1–V(2)–O(3)	92.49(14)	O(7)–V(1)–O(6)	108.31(18)
O(6)–V(2)–O(3)	164.34(13)	O(6)–V(1)–O(8)	109.45(14)
O(5)–V(2)–N(2)	92.63(18)	O(7)–V(1)–O(1)#2	105.4(2)
O(4)#1–V(2)–N(2)	162.52(15)	O(6)–V(1)–O(1)#2	111.16(17)
O(6)–V(2)–N(2)	90.79(14)	O(8)–V(1)–O(1)#2	112.04(17)
O(3)–V(2)–N(2)	87.37(14)	O(7)–V(1)–O(8)	110.4(2)
O(5)–V(2)–N(1)	166.60(17)	V(1)–O(8)–V(1)#4	166.8(4)
V(1)–O(6)–V(2)	156.1(2)		

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

Table 3  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for **1**.  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
V(2)	7150(1)	9145(1)	−472(1)	18(1)
V(1)	8279(1)	8260(1)	−2439(1)	20(1)
As(1)	5964(1)	9695(1)	1365(1)	23(1)
O(1)	7110(4)	10,991(5)	1597(2)	48(1)
O(2)	6361(4)	8566(4)	2217(2)	47(1)
O(5)	7887(4)	10,519(3)	−110(2)	33(1)
O(8)	10000	8467(6)	−2500	38(1)
O(7)	7893(4)	6682(4)	−2459(3)	42(1)
O(6)	8047(3)	8917(3)	−1488(2)	27(1)
O(4)	4428(3)	10,288(4)	1392(2)	33(1)
O(3)	6031(3)	8882(3)	435(2)	26(1)
N(1)	6472(4)	6924(4)	−746(2)	24(1)
N(2)	8667(4)	7940(4)	359(2)	24(1)
C(9)	5033(6)	5069(6)	−1345(4)	46(1)
C(6)	7994(7)	3776(6)	340(4)	48(2)
C(5)	9114(7)	4287(7)	895(4)	53(2)
C(8)	5861(7)	4170(6)	−829(4)	50(2)
C(12)	8477(4)	6567(5)	369(3)	26(1)
C(7)	7069(6)	4634(5)	−244(4)	37(1)
C(10)	5365(5)	6449(6)	−1291(3)	34(1)
C(4)	9390(5)	5699(6)	929(3)	37(1)
C(11)	7306(4)	6034(4)	−225(3)	24(1)
C(1)	9746(4)	8464(6)	918(3)	33(1)
C(2)	10,695(5)	7663(7)	1494(3)	46(1)
C(3)	10,514(5)	6302(7)	1502(3)	48(2)
H(1)	4247	4773	−1735	55
H(2)	7827	2849	341	58
H(3)	9712	3702	1261	64
H(4)	5642	3253	−856	60
H(7)	4787	7056	−1652	41
H(10)	11,136	5764	1889	58
H(11)	11,444	8059	1869	55
H(12)	9871	9398	925	39

### 3. Results and discussion

The single-crystal X-ray diffraction analysis reveals that compound **1** consists of a novel vanadium arsenate layer directly coordinated with *o*-phen ligands. The basic unit of compound **1** (see Fig. 1) shows the coordination environment around the vanadium and arsenic atoms. There are two crystallographically independent V atoms in this structure. The V(1) site exhibits a distorted tetrahedral coordination geometry with a terminal oxygen and three bridging oxygens which are linked with V(1), V(2), and As, respectively. The V(2) site exhibits the  $\{\text{VN}_2\text{O}_4\}$  octahedral geometry coordinated with two nitrogen donors of *o*-phen group, a terminal oxygen and three bridging oxygens, two of which are linked with V(1) and another linked with As. For  $\text{AsO}_4$  tetrahedron, three of the oxygen atoms are bridging to one V(1) atom and two V(2) atoms and the fourth oxygen atom is protonated with an As–O(2) distance of 1.698(3) Å (Table 2).

The structure of **1** consists of infinite double-chain ribbons along *a*-axis, as shown in Fig. 2a. In the double-ribbon, the  $\text{VO}_4$  tetrahedron,  $\text{AsO}_4$  tetrahedron and  $\text{VN}_2\text{O}_4$  octahedron connect with each other by conner-sharing oxygen atoms and form a spiral-shaped chain. Two adjacent chains are held together by the V2–O–As bond through the bridged oxygen atoms O4 to form the double-chain ribbon. There are alternating four-membered  $\{\text{V}_2\text{As}_2\text{O}_4\}$  and six-membered  $\{\text{V}_4\text{As}_2\text{O}_6\}$  rings in the double-chain ribbon. Moreover, two protonated oxygen sites O(2) exhibit a contact of 3.068 Å, indicating a H-bonding interaction between the two adjacent chains. Furthermore, the neighboring ribbons connect with each other by the V1–O8–V1 bond through the

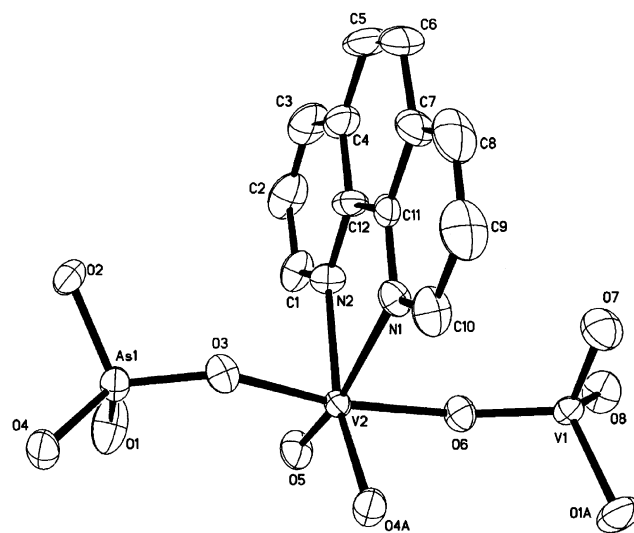


Fig. 1. View of the coordination environments of the vanadium and arsenic atoms, showing the atom-labeling scheme and 50% thermal ellipsoids.

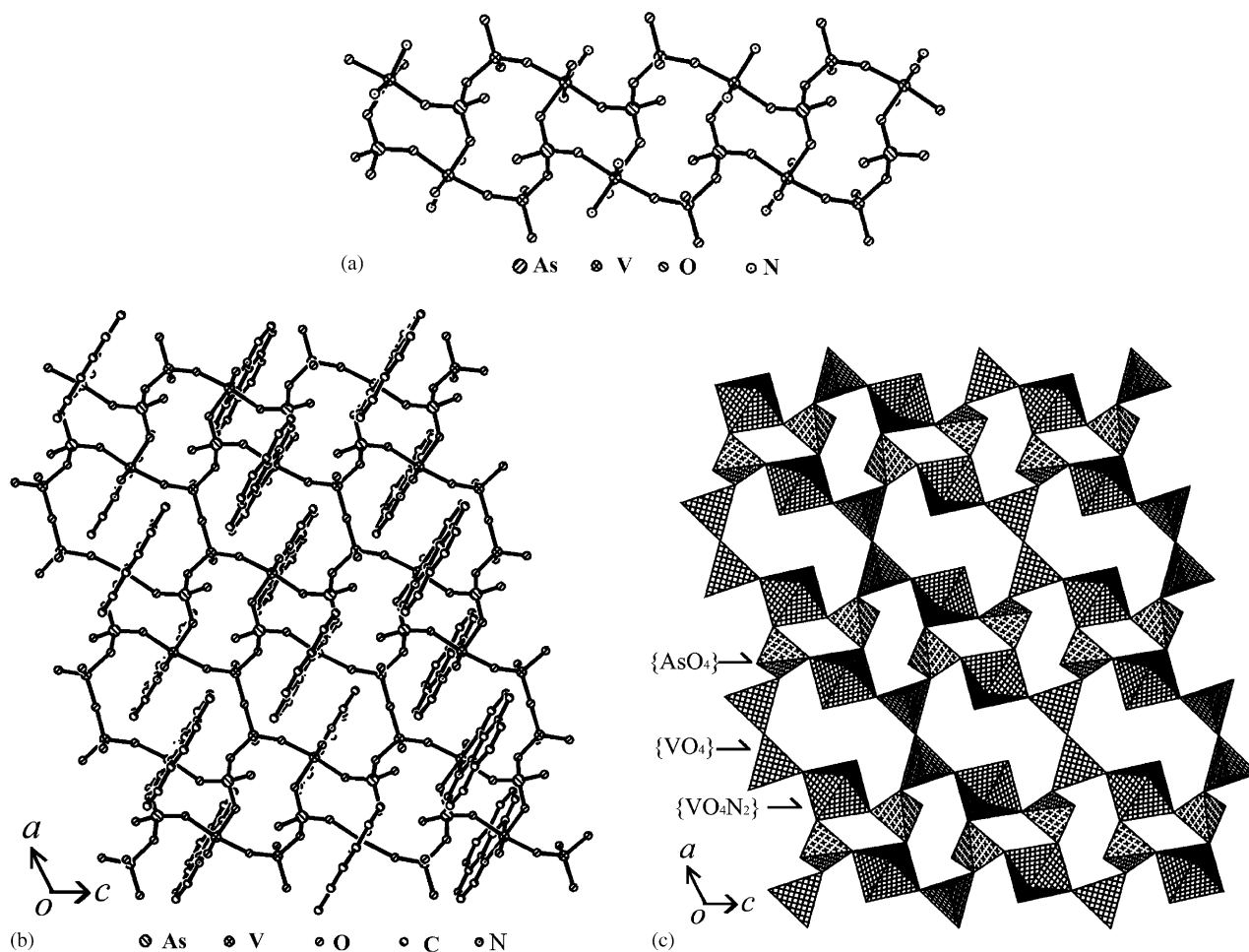


Fig. 2. (a) Section of infinite ribbons parallel in the structure of **1**. (b) View of the 2D layer structure of **1** on the *ac* plane. All hydrogen atoms are omitted for clarity. (c) The polyhedron representation of 2D layer in **1**. All carbon and hydrogen atoms are omitted for clarity.

corner-sharing VO<sub>4</sub> tetrahedron to produce a 2D network  $\{V_4O_7(HAsO_4)_2(o\text{-phen})_2\}_\infty$  lying the (010) plane (Fig. 2b). Eight-membered rings  $\{V_6As_2O_8\}$  are formed between neighboring double-chain ribbons. Therefore, the  $\{V_4O_7(HAsO_4)_2(o\text{-phen})_2\}_\infty$  layer may also be viewed as an extended 2D network structure with a 4,6,8-net. As far as we know, **1** is the first 2D layered vanadium arsenate constructed of 4,6,8-net sheets.

There are two kinds of  $\pi-\pi$  interactions in compound **1**, namely, within the same layer and between the adjacent layers. Similar to the structure of V<sub>3</sub>O<sub>7</sub>(phen) [21] [Co(phen)<sub>2</sub>V<sub>6</sub>O<sub>17</sub>] [22], and [Ni(phen)<sub>2</sub>V<sub>4</sub>O<sub>11</sub>] [23], the  $\pi-\pi$  stacking interaction between interlayer *o*-phen groups plays an important role in stabilization of the structure of **1** too. As shown in Fig. 3, the undulating vanadium arsenate layer of **1** is decorated with *o*-phen ligands projected above and below into the interlamellar region. The close contact distance between adjacent *o*-phen rings is 3.536 Å within the same layer and 3.429 Å between adjacent layers. Therefore, the 3D

supermolecular arrays are formed by  $\pi-\pi$  stacking interactions of the *o*-phen groups between adjacent layers.

Bond valence analysis shows that V(1) site is in the +5 oxidation state, while the V(2) site is in the +4 oxidation state. This result is also proved by ESR spectrum (as shown in Fig. 4) and X-ray photoelectron spectra (XPS) measurement (as shown in Fig. S2). The ESR spectrum of **1** at room temperature shows a V<sup>4+</sup> signal with  $g = 1.9656$ , in accordance with the bond valence sum calculations [24]. Furthermore, the bond valence sum calculations indicate that the AsO<sub>4</sub> tetrahedra are occupied by As<sup>5+</sup> ions. This oxidation state is consistent with the overall charge balance of the compound. To our knowledge, it is the first time that tetrahedral V(V) and octahedral V(IV) have been reported to occur concurrently in one vanadium arsenate compound.

In the IR spectrum of **1**, the strong bands at 912, 869, 773, 724 and 678 cm<sup>-1</sup> are due to the  $\nu(V=O)$  or  $\nu(V-O-V)$  vibrations. While the strong peak at



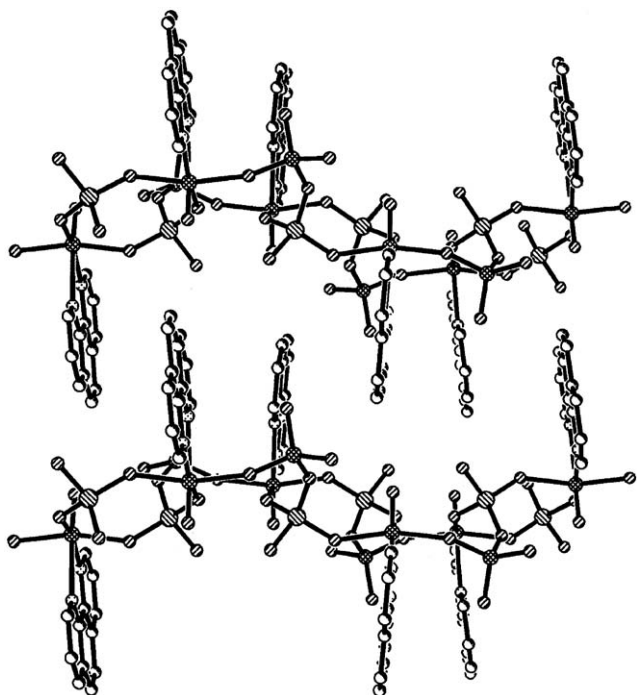


Fig. 3. The packing arrangement of **1** with 3D structure parallel to the vanadium arsenate layer.

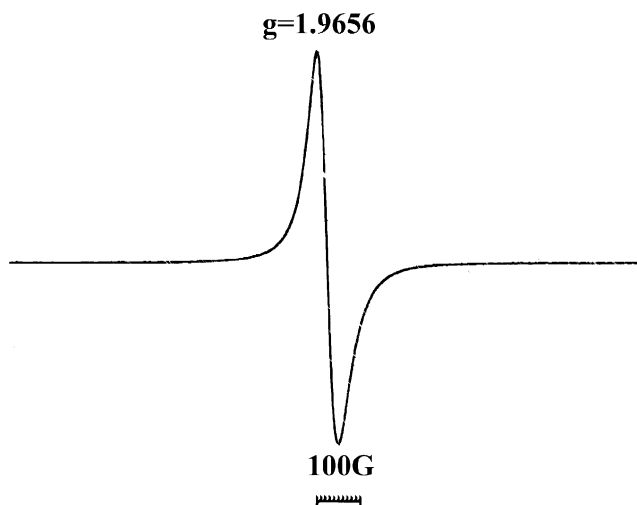


Fig. 4. The ESR spectrum of **1**.

$981\text{ cm}^{-1}$  is attributed to the vibrations of As–O bands. Bands in the  $1627\text{--}1139\text{ cm}^{-1}$  region are attributed to characteristic peaks of *o*-phen groups. The broad band in  $3430\text{ cm}^{-1}$  can be attributed to O–H stretching.

The TG curve of compound **1** (Fig. 5) exhibits three steps of weight losses. The first weight loss occurs in the range of  $320\text{--}390^\circ\text{C}$ , corresponding to the removal of  $\text{H}_2\text{O}$  from  $\text{HAsO}_4$ . The observed weight loss (1.95%) is consistent with the calculated value (1.88%). The second weight loss is 13.35% from  $400^\circ\text{C}$  to  $455^\circ\text{C}$ , the third is 24.86% in the temperature range  $455\text{--}600^\circ\text{C}$ ,

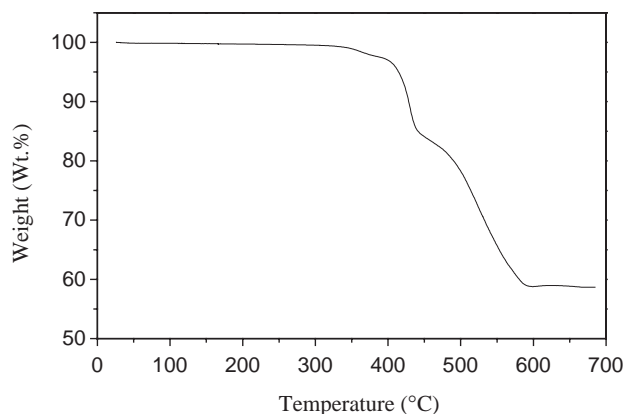


Fig. 5. The TG curve of **1**.

both assigned to the loss of *o*-phen groups. The observed weight loss in the second and third step (38.21%) is in agreement with the calculated value (37.70%). The sample does not lose weight at temperatures higher than  $600^\circ\text{C}$ .

In conclusion, we have prepared a novel layered vanadium arsenate with a directly coordinated *o*-phen ligand. The successful isolation of **1** further confirms the function of organic structure-directing agents for “tailoring” the microstructures of vanadium arsenate. This work also shows that the hydrothermal synthesis is a powerful method to obtain novel structural materials.

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