

Synthesis and Crystal Structure of the Bimetallic Complex [Fe(phen)₃]₂[phen][V₄O₁₂]·19H₂O

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A new bimetallic complex, [Fe(phen)₃]₂[phen][V₄O₁₂]·19H₂O (**1**) has been obtained under non-hydrothermal conditions and characterized by single-crystal X-ray diffraction, IR and TG analysis. Crystal data: Fe₂V₄O₃₁N₁₄C₈₄H₉₄, triclinic, *PI*, *a* = 12.920(5), *b* = 17.833(5), *c* = 23.420(5) Å, *α* = 107.119(5)°, *β* = 90.643(5)°, *γ* = 107.643(5)°, *Z* = 2. In compound **1**, water molecules build up 1D chains and decameric rings by hydrogen bonds. The hydrogen bond interactions between decameric rings and 1D chains form a 2D supramolecular sheet with large holes. The [V₄O₁₂]⁴⁻ anions fill these holes. The [Fe(phen)₃]²⁺ cations play a role as charge-compensating and space-filling units. Hydrogen bonding and electrostatic interactions lead to a new 3D supramolecular framework.

Key words: Non-hydrothermal Synthesis, Vanadium Oxide, Bimetallic Compound, Crystal Structure, 2D Water Sheet

Introduction

In recent years, there has been extensive interest in inorganic-organic hybrid vanadium oxides for their structural diversity and potential applications in the fields of catalysis, electrical conductivity, magnetism, and photochemistry [1–5]. Isopolyoxovanadate anions have widely been used to support inorganic-organic hybrid complexes because the vanadium cations can adopt a variety of coordination geometries in various oxidation states. In this field, the [V₄O₁₂]⁴⁻ anion has been widely studied because it can exist in chair-like and classical configurations. When the [V₄O₁₂]⁴⁻ anion is attached to bimetallic complex cations *via* the bridging O atoms, it is inclined to use two terminal O atoms from two adjacent vanadium atoms to form a chair-like configuration [6]. If it is isolated, it forms a classical configuration. Known examples for such bimetallic complexes with discrete [V₄O₁₂]⁴⁻ anion structures include [Ni(phen)₃]₂[V₄O₁₂]·17.5H₂O [6], [Co(phen)₃]₂[phen][V₄O₁₂]·22H₂O [7], [Ni(phen)₃]₂[phen][V₄O₁₂]·22H₂O [7], [N(C₄H₉)₄]₃HV₄O₁₂ [8], [Ni(2,2'-bipy)₃]₂[V₄O₁₂]·11H₂O [9], [Zn(2,2'-bipy)₃]₂[V₄O₁₂]·11H₂O [10], [Cu(phen)₃]₂[phen][V₄O₁₂]·22H₂O [11], and [Zn(phen)₃]₂[V₄O₁₂]·20H₂O [12]. Even though the num-

ber of compounds with [V₄O₁₂]⁴⁻ units is not any more limited, cases that contain iron-bimetallic complexes are still very scarce in the literature. To the best of our knowledge, there was only one example reported, that is [Fe(2,2'-bipy)₃]₂[V₄O₁₂]·10H₂O [13].

In the present work we tried to change the reaction conditions or the nitrogen donor chelating ligand, and expected to gain a new compound. We utilized non-hydrothermal synthesis methods to obtain a unique iron complex [Fe(phen)₃]₂[phen][V₄O₁₂]·19H₂O (**1**), and report its structure. It consists of [V₄O₁₂]⁴⁻ anions, [Fe(phen)₃]²⁺ complexes, free (uncoordinated) phen molecules, and water molecules. The water molecules form a 2D water sheet *via* hydrogen bonds. There are large holes in the 2D water sheet, which are filled with the [V₄O₁₂]⁴⁻ units. The free phen molecules are fixed in the crystal by hydrogen bonds. The [Fe(phen)₃]²⁺ cations fill the interlayer space as charge-compensating and space-filling units.

Results and Discussion

Structure description

The X-ray crystallographic study has shown that the fundamental building units of compound **1** include

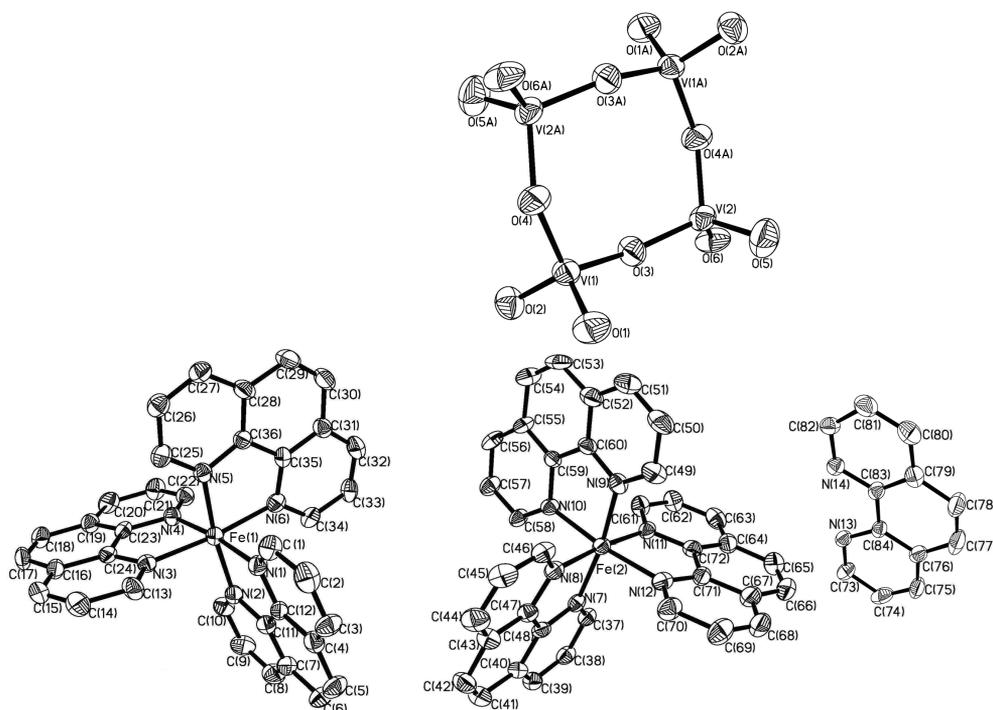


Fig. 1. Molecular structures of the principal components of **1** in the crystal (above: the tetrameric vanadate anion; below: the two crystallographically independent $[\text{Fe}(\text{phen})_3]^{2+}$ cations and the uncoordinated phen molecule; H atoms were omitted for clarity).

Table 1. Selected bond lengths (Å) and angles (deg) for $[\text{Fe}(\text{phen})_3]_2[\text{phen}][\text{V}_4\text{O}_{12}] \cdot 19\text{H}_2\text{O}$.

Bond lengths			
Fe(1)–N(1)	1.982(7)	V(1)–O(4)	1.783(7)
Fe(1)–N(4)	1.987(7)	V(1)–O(3)	1.800(6)
Fe(1)–N(3)	1.988(7)	V(1)–O(1)	1.643(7)
Fe(1)–N(6)	1.998(7)	V(2)–O(6)	1.615(7)
Fe(1)–N(2)	1.999(7)	V(2)–O(5)	1.667(7)
Fe(1)–N(5)	2.005(7)	V(2)–O(3)	1.799(6)
V(1)–O(2)	1.636(7)	V(2)–O(4) ^{#1}	1.800(7)
Angles			
N(1)–Fe(1)–N(4)	173.2(3)	N(3)–Fe(1)–N(2)	93.1(3)
N(1)–Fe(1)–N(3)	92.3(3)	N(6)–Fe(1)–N(2)	92.5(3)
N(4)–Fe(1)–N(3)	83.7(3)	N(1)–Fe(1)–N(5)	93.9(3)
N(1)–Fe(1)–N(6)	91.0(3)	N(4)–Fe(1)–N(5)	91.7(3)
N(4)–Fe(1)–N(6)	93.5(3)	N(3)–Fe(1)–N(5)	92.6(3)
N(3)–Fe(1)–N(6)	173.9(3)	N(6)–Fe(1)–N(5)	82.1(3)
N(1)–Fe(1)–N(2)	82.7(3)	N(2)–Fe(1)–N(5)	173.5(3)
N(4)–Fe(1)–N(2)	92.1(3)	O(6)–V(2)–O(5)	109.5(4)
O(2)–V(1)–O(1)	109.6(4)	O(6)–V(2)–O(3)	108.7(4)
O(2)–V(1)–O(4)	108.8(3)	O(5)–V(2)–O(3)	112.3(4)
O(1)–V(1)–O(4)	107.8(4)	O(6)–V(2)–O(4) ^{#1}	107.8(3)
O(2)–V(1)–O(3)	110.4(3)	O(5)–V(2)–O(4) ^{#1}	108.4(4)
O(1)–V(1)–O(3)	110.0(4)	O(3)–V(2)–O(4) ^{#1}	110.0(3)
O(4)–V(1)–O(3)	110.3(3)	V(2)–O(3)–V(1)	157.0(4)

an isolated polyanion $[\text{V}_4\text{O}_{12}]^{4-}$, two $[\text{Fe}(\text{phen})_3]^{2+}$ cations, a free phen molecule, and water molecules (Fig. 1). The Fe(II) center exhibits an octahedral coordination geometry defined by six nitrogen atoms from three phen ligands. The Fe–N distances range from 1.979 to 2.019 Å, and the angles N–Fe–N are in the range 82.1–83.7° (Table 1). The isolated $[\text{V}_4\text{O}_{12}]^{4-}$ anion has an eight-membered $\{\text{V}_4\text{O}_4\}$ ring structure. Each vanadium atom is linked to two bridging O atoms (O_b) and two terminal O atoms (O_t) and exhibits a distorted VO_4 tetrahedral geometry. The bond lengths V–O are in the ranges 1.615(7)–1.796(6) Å and 1.771(6)–1.800(6) Å for V– O_t and V– O_b , respectively, while the angles O–V–O are in the range 107.1(3)–112.3(4)° (Table 1).

In compound **1**, the water molecules are interconnected through hydrogen bonds running along the crystallographic *a* and *b* axes to form an infinite 2D sheet (Fig. 2). The sheet with large holes consists of decameric water rings and 1D chains with hydrogen bond interactions among O9W, O13W and O14W. The 1D chain is built up from O9W, O4W, O1W, and O2W. The water molecule O8W is connected to O2W and

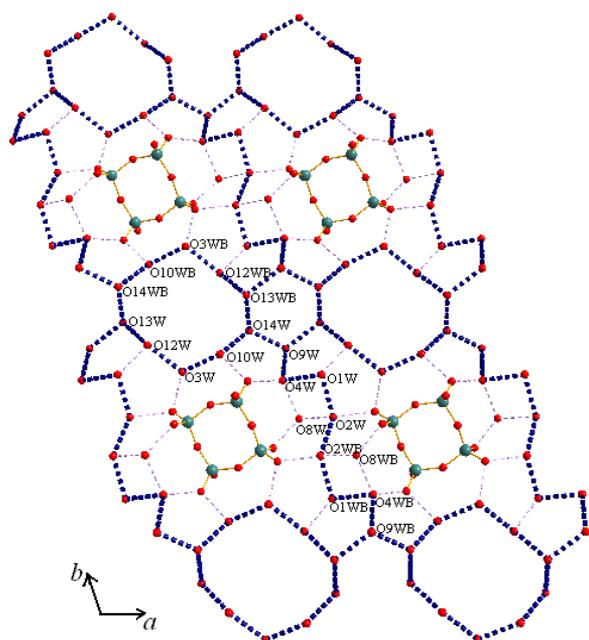


Fig. 2. A schematic illustration of the 2D water sheet of compound **1**. The hydrogen bonds of this sheet are highlighted by thick dashed lines, those involving $[\text{V}_4\text{O}_{12}]^{4-}$ are shown with thin dashed lines.

O4W of the chain through additional hydrogen bonds. O2W acts as a junction of two 1D chains by O2W·O2WB bonds with a distance of 2.940(5) Å. The decamers with a boat-chair-boat conformation are constructed by O14W, O13W, O12W, O3W, and O10W and their symmetry equivalents. The size of the voids

in the sheets is 10.422×14.062 Å, and is filled with $[\text{V}_4\text{O}_{12}]^{4-}$ anions. The 2D sheet is further stabilized by the existence of hydrogen bonds between the water molecules and O_t atoms of the $[\text{V}_4\text{O}_{12}]^{4-}$ anions. Between adjacent decamers, there are hexameric rings of water molecules with a chair-like configuration, which are formed by O9W, O13W, O14W and their symmetry counterparts. The average OW·OW distance is 2.837 Å, which is slightly shorter than that present in liquid water (2.854 Å) [14] and closer to that in the ice II phase (2.77–2.84 Å) [15]. The 2D water sheet is similar to that in compound $[\text{Zn}(\text{phen})_3]_2 \cdot [\text{V}_4\text{O}_{12}] \cdot 20\text{H}_2\text{O}$ [12], but also contains hexameric water rings and 1D chains.

The existence of centrosymmetrically related hydrogen bonds in chair-like hexamers brings about disordering of most of the hydrogen atoms. If one of these atoms acts as hydrogen bond donor, then its symmetry related partner should also donate back a hydrogen atom. The resulting tandem hydrogen bond is highly improbable and its existence has never been proven. More stable configurations are obtained if the hydrogen atoms are disordered over two equally occupied sites so that only one hydrogen atom is involved in a given hydrogen bond [16]. Therefore, it has not been possible to refine the hydrogen occupation factors in compound **1**.

The free (uncoordinated) phen molecule is linked with the 2D sheets by hydrogen bonds (Fig. 3), and the $[\text{Fe}(\text{phen})_3]^{2+}$ complex cation acts as charge-compensating and space-filling unit between the layers

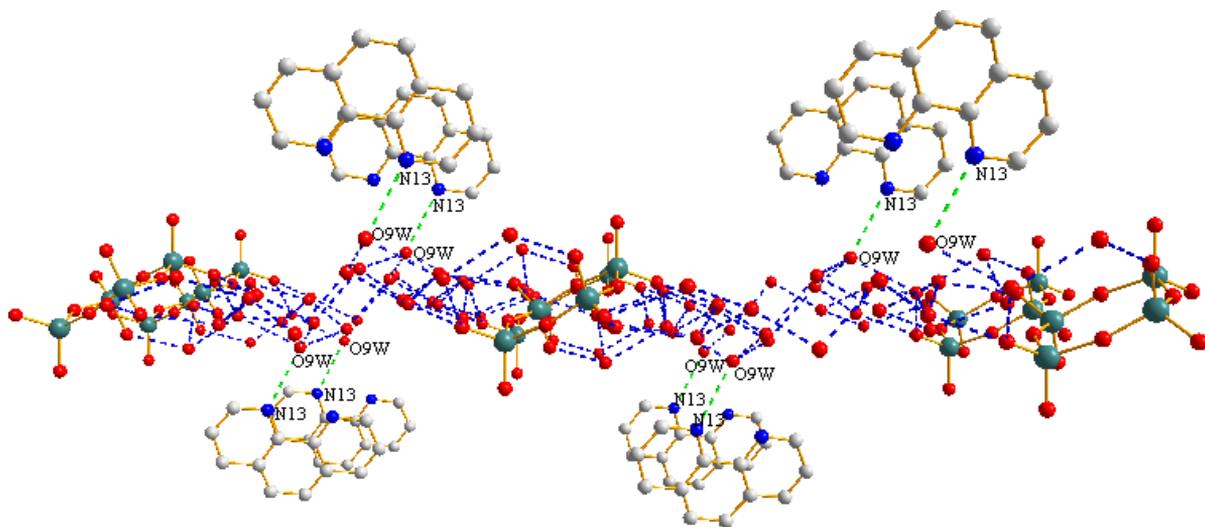


Fig. 3. View of the hydrogen bonds between the free phen molecules and the 2D water sheet.

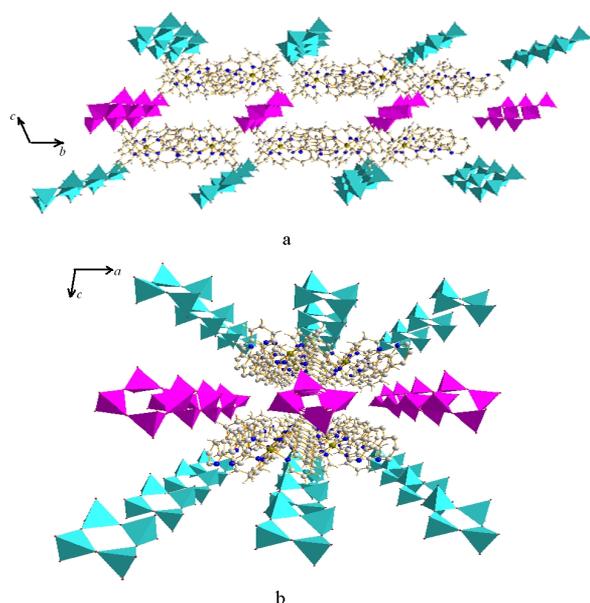


Fig. 4. View of the 3D-framework of compound **1**. (a) The extended structure viewed along the *a* axis, (b) the extended structure viewed along the *b* axis. The blue and light-purple tetrahedra represent $[\text{V}_4\text{O}_{12}]^{4-}$ anions in different sheets (color online).

via hydrogen bonds and electrostatic interactions to form a 3D supramolecular framework (Fig. 4).

IR spectrum of compound **1**

The IR spectrum of compound **1** has strong bands at 906 and 849 cm^{-1} due to the terminal V–O stretching modes. The bands at 789, 706 and 677 cm^{-1} are attributed to symmetrical and asymmetrical V–O–V stretching. Bands at 1420, 1510, 1550, 1560, and 1640 cm^{-1} are other characteristic vibrations of phen.

Thermal analysis

In the TG curve of compound **1** there are four steps of weight loss. The first step, in the range 45–140 °C, is ascribed to the loss of water from the crystal. The observed weight loss (17.1 %) is in agreement with the calculated value (16.2 %). The second step, weight loss of 8.8 % in the range 167–245 °C, corresponds to the loss of free phen molecules (calcd. 8.5 %). The final two continuous steps occur between 300 and 520 °C and are due to the loss of coordinated phen molecules (50.3 % observed, 51.2 % calcd.).

In summary, a new bimetallic complex, $[\text{Fe}(\text{phen})_3]_2[\text{phen}][\text{V}_4\text{O}_{12}] \cdot 19\text{H}_2\text{O}$ (**1**) has been synthesized under non-hydrothermal conditions. It con-

Table 2. Details of data collection and structure refinement for compound **1**.

Formula	$\text{C}_{84}\text{H}_{94}\text{Fe}_2\text{N}_{14}\text{O}_{31}\text{V}_4$
M_r	2111.19
Cryst. size, mm^3	$0.18 \times 0.15 \times 0.11$
Crystal system	triclinic
Space group	$P\bar{1}$
<i>a</i> , Å	12.920
<i>b</i> , Å	17.833
<i>c</i> , Å	23.420
α , deg	107.119(5)
β , deg	90.643(5)
γ , deg	107.643(5)
<i>V</i> , Å ³	4884(3)
<i>Z</i>	2
D_{calcd} , g cm^{-3}	1.435
$F(000)$, e	2176
$\mu(\text{MoK}\alpha)$, mm^{-1}	0.737
<i>hkl</i> range	$-15 \leq h \leq 15, -18 \leq k \leq 21, -25 \leq l \leq 27$
θ_{max} , deg	25.0
Refl. collected / unique	25141 / 17029
R_{int}	0.052
Data / parameters	17029 / 1157
GoF (F^2)	0.950
$R1 / wR2 [I > 2\sigma(I)]$	0.074 / 0.162
$R1 / wR2$ (all data)	0.198 / 0.216
Largest diff. peak / hole, e \AA^{-3}	1.77 / -0.48

tains a 2D water sheet with big holes and $[\text{V}_4\text{O}_{12}]^{4-}$ anions filled in these voids. The $[\text{Fe}(\text{phen})_3]^{2+}$ complex cations are charge-compensating and space-filling units. The 3D supramolecular framework is formed by hydrogen bonds and electrostatic interactions.

Experimental Section

General methods and materials

All reagents were purchased commercially and used without further purification. Deionized water was used for the synthesis of the target compound. The infrared spectrum was recorded on a Nicolet 170SX FT-IR spectrophotometer with a KBr pellet in the 4000–400 cm^{-1} region. TG analysis was performed on a Netzsch STA 449C microanalyzer in an atmosphere of nitrogen with a heating rate of 10 °C min^{-1} in the temperature range 25–600 °C.

Synthesis

$[\text{Fe}(\text{phen})_3]_2[\text{phen}][\text{V}_4\text{O}_{12}] \cdot 19\text{H}_2\text{O}$ (**1**)

$\text{NaVO}_3 \cdot \text{H}_2\text{O}$ (0.033 g, 0.2 mmol) was dissolved in deionized water (20 mL). The solution was heated to 80 °C with stirring, and simultaneously, the pH value of this solution was carefully adjusted to about 10 with a dilute NaOH solution (1 M). $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ (0.032 g, 0.2 mmol) and phen- H_2O (0.04 g, 0.2 mmol) were dissolved in hot deionized water

(10 mL), and the resulting solution was added dropwise to the vanadium containing solution with stirring. The mixture was heated and stirred for 0.5 h at 80 °C. After it had cooled to r. t., the red suspension was filtered to remove insoluble solids and allowed to evaporate slowly. After one week, red sheet-like crystals suitable for X-ray diffraction were isolated. – C₈₄H₉₄Fe₂N₁₄O₃₁V₄: calcd. Fe 5.30, V 9.67, C 47.77, H 4.45, N 9.29; found Fe 5.71, V 10.02, C 47.36, H 4.11, N 9.01.

Crystal structure determination

Single crystal X-ray diffraction intensities for compound **1** were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$)

at 293 K. Absorption correction was applied using a multi-scan technique. The structure was solved by Direct Methods (SHELXS-97 [17]) and refined by full-matrix least-squares on F^2 (SHELXL-97 [18]). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to phen were treated as rigid groups. Most hydrogen atoms of water molecules could not be positioned reliably. Additional details of data collection and structure refinement are listed in Table 2, and displacement ellipsoid plots of the principal components of **1** are given in Fig. 1. Selected bond lengths and angles are listed in Table 1.

CCDC 687323 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.

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