

两个具有相似{V₁₀}阴离子骨架的化合物的合成和结构表征

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本文描述了两个具有相似阴离子骨架的化合物, [Na₂(H₂O)₁₀(NH₄)₄][V₁₀O₂₈] (**1**) 和 [Na₂(H₂O)₁₀(NH₄)₄][V₉MoO₂₈] (**2**)。化合物 **1** 的阴离子是一个常见的钒十骨架, 而化合物 **2** 与化合物 **1** 是同晶异质体, 化合物 **2** 的阴离子是混有一个钼原子的钒十骨架。X-射线晶体结构测定表明, 这两个化合物均属于三斜晶系, *P* $\bar{1}$ 空间群。晶胞参数分别为化合物 **1**: *a* = 0.86024(4) nm, *b* = 1.04561(5) nm, *c* = 1.12828(4) nm, α = 68.833(1)°, β = 87.158(1)°, γ = 67.065(1)°; 化合物 **2**: *a* = 0.86511(3) nm, *b* = 1.04549(5) nm, *c* = 1.12446(5) nm, α = 69.071(1)°, β = 87.145(1)°, γ = 66.982(1)°。

关键词: 多金属氧酸盐化学 钒十骨架 水热合成
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Syntheses and Structural Characterizations of Two Compounds Containing Similar Backbone Anion {V₁₀}

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Two compounds with similar anion backbone, [Na₂(H₂O)₁₀(NH₄)₄][V₁₀O₂₈] (**1**) and [Na₂(H₂O)₁₀(NH₄)₄][V₉MoO₂₈] (**2**), are described. The anion of **1** is of decavanadate with normal structure, while the anion of **2** has a molybdenum atom mixing with four vanadium atoms at certain positions in the similar backbone of the decanucleus structure. Crystal data for H₃₆N₄O₃₈Na₂V₁₀ (**1**): triclinic, space group *P* $\bar{1}$, *a* = 0.86024(4) nm, *b* = 1.04561(5) nm, *c* = 1.12828(4) nm, α = 68.833(1)°, β = 87.158(1)°, γ = 67.065(1)°, *V* = 0.86665(7) nm³, *Z* = 1, *M_r* = 1255.71, *D_c* = 2.406 g · cm⁻³, *F*(000) = 620, μ (Mo *K*α) = 2.719 mm⁻¹. Crystal data for H₃₆N₄O₃₈Na₂V₉Mo (**2**): triclinic, space group *P* $\bar{1}$, *a* = 0.86511(3) nm, *b* = 1.04549(5) nm, *c* = 1.12446(5) nm, α = 69.071(1)°, β = 87.145(1)°, γ = 66.982(1)°, *V* = 0.86951(6) nm³, *Z* = 1, *M_r* = 1300.71, *D_c* = 2.484 g · cm⁻³, *F*(000) = 639, μ (Mo *K*α) = 2.802 mm⁻¹. CSD: **1**, 413132, **2**, 413133.

Keywords: polyoxometalatic chemistry decavanadate hydrothermal synthesis

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0 Introduction

The polyoxometalatic chemistry has a long history, however, they have still attracted much attention from chemists and physicists owing to their varied applications in many fields, such as analytical and clinical chemistry, catalysis, biochemistry, medicine, and solid-state devices^[1]. The polyoxovanadates compose an important part of the polyoxometalates, and of which the decavanadate anion formed normally from acidic aqueous solution is very popular. The structure of the decavanadate anion can be described as that six VO_6 octahedra form a plane with two VO_6 octahedra above and two below the plane via edged-sharing^[2]. According to various protonation degrees, the reported decavanadate polyanions have following types: $[\text{V}_{10}\text{O}_{28}]^{6-}$, $[\text{HV}_{10}\text{O}_{28}]^{5-}$, $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$, $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$, $[\text{H}_4\text{V}_{10}\text{O}_{28}]^{2-}$, in which only three types polyoxovanadate anions ($[\text{V}_{10}\text{O}_{28}]^{6-}$, $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$, $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$) seem to be stable in solid state. Many compounds with different cations have been reported, such as $\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$ ^[3], $\text{Ca}_3\text{V}_{10}\text{O}_{28} \cdot 17\text{H}_2\text{O}$ ^[4], $\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$ ^[5], $[(\text{C}_5\text{H}_5\text{NH})_6(\text{V}_{10}\text{O}_{28})]^{12-}$, $[(\text{C}_6\text{H}_7\text{NH})_6(\text{V}_{10}\text{O}_{28})]^{12-}$, $[(\text{C}_5\text{H}_5\text{NH})_4(\text{H}_2\text{V}_{10}\text{O}_{28})]^{12-}$, $[(\text{C}_7\text{H}_9\text{NH})_4(\text{H}_2\text{V}_{10}\text{O}_{28})]^{12-}$, $[(\text{CH}_3)_4\text{N}]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]^{12-}$, $[(\text{C}_2\text{H}_5)_4\text{N}_3][\text{H}_3\text{V}_{10}\text{O}_{28}]^{11-}$, $[(\text{C}_6\text{H}_7\text{NH})_3][\text{H}_3\text{V}_{10}\text{O}_{28}] \cdot \text{H}_2\text{O}$ ^[6], $[(\text{C}_7\text{H}_9\text{NH})_3][\text{H}_3\text{V}_{10}\text{O}_{28}] \cdot \text{H}_2\text{O}$ ^[7], $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{H}_4\text{V}_{10}\text{O}_{28}]^{10-}$, $(\text{NH}_4)_4[\text{H}_4\text{V}_{10}\text{O}_{28}][\text{N}(\text{CH}_2\text{CH}_2\text{COOH})_3]_2 \cdot 4\text{H}_2\text{O}$ ^[8]. Herein we report syntheses and characterizations of two compounds belonging to $[\text{V}_{10}\text{O}_{28}]^{6-}$ family.

1 Experimental

1.1 Syntheses

Compound 1: An aqueous mixture of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (1.0g, 4.1mmol), NH_4VO_3 (0.2g, 1.7mmol), $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ (1.9g, 18.1mmol), $\text{CH}_3\text{COONH}_4$ (0.6g, 7.8mmol) in 10mL H_2O was heated at 150°C under autogenous pressure for 60h in a sealed 30mL Teflon-linked stainless steel vessel. A solid phase was filtered off, and the filtrate was allowed to stand in open air at ambient temperature. Orange crystals suitable for X-ray diffraction study were isolated after three

days (30% yield based on V). Elemental analysis: Calc. (%) for $\text{H}_{36}\text{N}_4\text{O}_{38}\text{Na}_2\text{V}_{10}$, H, 2.89; N, 4.46; O, 48.42; Na, 3.66; V, 40.57. Found(%): H, 2.95; N, 4.50; O, 48.38; Na, 3.69; V, 40.61%.

Compound 2: To a mixture solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (1.4g, 5.8mmol), NH_4VO_3 (0.7g, 6.0mmol), $\text{CH}_3\text{COONH}_4$ (1.0g, 13.0mmol) and $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ (0.2g, 1.9mmol) in 10mL H_2O and 50% acetic acid (5mL, pH (4.20) was added 5mL DMSO and the resultant was allowed to stand in open air at ambient temperature. Dark green crystals of **2** were isolated after a week (70% yield based on V). Elemental analysis: Calc. (%) for $\text{H}_{36}\text{N}_4\text{O}_{38}\text{Na}_2\text{V}_9\text{Mo}$, H, 2.79; N, 4.31; O, 46.74; Na, 3.53; V, 35.25; Mo, 7.38. Found(%): H, 2.86; N, 4.25; O, 46.80; Na, 3.50; V, 35.21; Mo, 7.42.

1.2 Structure Determination

Two sets of data for **1** and **2** with approximate dimensions of 0.28mm × 0.23mm × 0.21mm for **1** and 0.31mm × 0.26mm × 0.24mm for **2** were collected on a Siemens Smart CCD diffractometer equipped with graphite-monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.071073$ nm) at room temperature. The structures were solved by direct methods and succeeding difference fourier syntheses, and then refined by full-matrix least-squares method anisotropically for all metal atoms and coordinative oxygen atoms. All calculations were performed by using SHELXTL-97 program package^[9].

Compound 1: A total of 4521 reflections were collected in the range of $1.95^\circ < \theta < 25.01^\circ$, of which 3030 ($R_{\text{int}} = 0.0193$) were unique ($I > 2\sigma(I)$), the final convergence indices $R = 0.0595$ and $wR = 0.1718$ ($w = 1/[\sigma^2(F_o^2) + (0.0800P)^2 + 8.35P]$ where $P = (\max(F_o^2, 0) + 2F_c^2)/3$), $S = 1.097$, and $(\Delta/\sigma)_{\text{max}} = 0.000$. The maximum and minimum residual peaks on the final difference Fourier map are $1126e \cdot \text{nm}^{-3}$ and $-1236e \cdot \text{nm}^{-3}$, respectively. CSD: 413132.

Compound 2: A total of 4166 reflections were collected in the range of $1.95^\circ < \theta < 24.00^\circ$, of which 2718 ($R_{\text{int}} = 0.0186$) were unique ($I > 2\sigma(I)$), the final convergence indices $R = 0.0542$ and

$wR = 0.1964$ ($w = 1/[\sigma_2(F_o^2) + (0.1340P)^2 + 8P]$)
 where $P = (\max(F_o^2, 0) + 2F_c^2)/3$, $S = 1.005$, and
 $(\Delta/\sigma)_{\max} = 0.005$. The maximum and minimum residual peaks on the final difference Fourier map are $653e \cdot nm^{-3}$ and $-1179e \cdot nm^{-3}$, respectively. CSD: 413133.

The crystal data and experimental details are given in Table 1.

2 Results and Discussion

The X-ray structural analyses of compounds **1** and **2** reveal that both anions of the compounds have the same backbone structures (Fig. 1). The decavanadate anion can be described as ten tetragonal bipyramidal VO_6 are connected *via* edge-sharing and corner-sharing modes. According to different positions in one of the anion, there are three types of vanadium atoms: (I) four V atoms are located above and below the equatorial

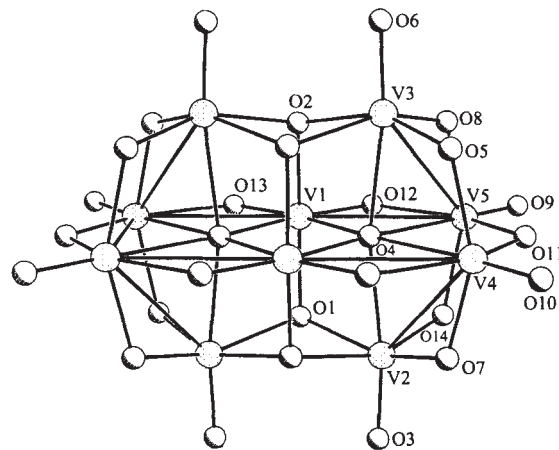


Fig. 1 Ball-and-stick figure of $[V_{10}O_{28}]$ anion

plane (V_2 , V_3 and their symmetry equivalent atoms); (II) four V atoms are located on the equatorial plane (V_4 , V_5 and their symmetry equivalent atoms); (III) two central vanadium atoms are on the equatorial plane (V_1 and its symmetry equivalent atom). Similarly,

Table 1 Crystal Data and Experimental Details of Compounds **1** and **2**

	1	2
empirical formula	$H_{36}N_4O_{38}Na_2V_{10}$	$H_{36}N_4O_{38}Na_2V_9Mo$
color and habit	orange yellow block	dark green
crystal size/ mm^3	$0.28 \times 0.23 \times 0.21$	$0.31 \times 0.26 \times 0.24$
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/nm	0.86024(4)	0.86511(3)
b/nm	1.04561(5)	1.04549(5)
c/nm	1.12828(4)	1.12446(5)
$\alpha/^\circ$	68.8330(10)	69.0710(10)
$\beta/^\circ$	87.1580(10)	87.1450(10)
$\gamma/^\circ$	67.0650(10)	66.9820(10)
volume/ nm^3	0.86665(7)	0.86951(6)
Z	1	1
formula weight	1255.71	1300.71
density(cal.)/($g \cdot cm^{-3}$)	2.406	2.484
absorption coefficient/ mm^{-1}	2.719	2.802
$F(000)$	620	639
θ range/ $^\circ$	1.95 to 25.01	1.95 to 24.00
reflections measured	4521	4166
index ranges of measured data	$-10 \leq h \leq 7, -12 \leq k \leq 2, -13 \leq l \leq 13$	$-9 \leq h \leq 9, -11 \leq k \leq 11, -12 \leq l \leq 12$
independent reflections	3030 ($R_{int} = 0.0193$)	2718 ($R_{int} = 0.0186$)
observed reflection	2753 ($> 2\sigma(I)$)	2649 ($> 2\sigma(I)$)
parameter/restraints/data(obs.)	244 / 0 / 2753	263 / 0 / 2649
final R indices (obs.)	$R_1 = 0.0595, wR_2 = 0.1718$	$R_1 = 0.0542, wR_2 = 0.1964$
R indices (all)	$R_1 = 0.0650, wR_2 = 0.1779$	$R_1 = 0.0555, wR_2 = 0.1976$
goodness-of-fit	1.097	1.005
largest and mean Δ/σ	0.000, 0.000	0.005, 0.001
largest difference peak/($e \cdot nm^{-3}$)	1126, -1236	653, -1179

according to the coordinative conditions, the oxygen atoms in each anion can be classified: (I) eight terminal O, with V-O distances of 0.1613 ~ 0.1653 nm; (II) fourteen μ_2 -O (V-O: 0.1688 ~ 0.2102nm); (III) four μ_3 -O (V-O: 0.1924 ~ 0.2093nm); (IV) two μ_6 -O (V-O: 0.2121 ~ 0.2374nm). Tables 2 and 3 list the selective bond lengths and bond angles of **1** and **2**, respectively.

By means of the empirical bond length/bond number calculation[10], $s = (R/1.79)^{-5.1}$ ($R = \text{V-O distance}$; $s = \text{bond number}$), the protonation sites were also confirmed. Tables 4 and 5 list the bond numbers

for selective oxygen atoms of **1** and **2**, respectively, which reveal that none of oxygen atoms is protonated and both anions of the backbones belong to $[\text{V}_{10}\text{O}_{28}]^{6-}$ type.

According to structural analysis, there is a Mo atom to occupy one of four positions (V_2 , V_3 and their symmetry equivalents) in anion of **2** randomly, which was confirmed by atomic absorption analysis and the different colour appearance of **2** from **1**, although **2** has the same unit cell parameters with **1**. There are eight lines appearing in the EPR of **2** which indicates that four valence V atom must exist (Fig. 2), and the dark

Table 2 Selected Bond Lengths(nm) and Bond Angles($^\circ$) of Compound **1**

V(1)-O(10)	0.1691(5)	V(2)-O(12)#1	0.2066(5)	V(4)-O(8)	0.1882(5)
V(1)-O(11)	0.1697(5)	V(2)-O(14)#1	0.2240(4)	V(4)-O(5)#1	0.1912(5)
V(1)-O(12)	0.1924(5)	V(3)-O(3)	0.1618(5)	V(4)-O(10)	0.2092(5)
V(1)-O(13)	0.1929(5)	V(3)-O(8)	0.1813(5)	V(4)-O(14)	0.2307(4)
V(1)-O(14)	0.2121(4)	V(3)-O(9)	0.1828(5)	V(5)-O(1)	0.1618(6)
V(1)-O(14)#1	0.2128(4)	V(3)-O(12)#1	0.2005(5)	V(5)-O(6)#1	0.1862(5)
V(2)-O(7)	0.1634(5)	V(3)-O(13)	0.2044(5)	V(5)-O(9)#1	0.1909(5)
V(2)-O(4)	0.1799(5)	V(3)-O(14)	0.2268(4)	V(5)-O(4)	0.1910(5)
V(2)-O(5)	0.1821(5)	V(4)-O(2)	0.1613(5)	V(5)-O(11)	0.2055(5)
V(2)-O(13)	0.2003(5)	V(4)-O(6)	0.1823(5)	V(5)-O(14)#1	0.2372(4)
O(10)-V(1)-O(11)	106.5(2)	O(7)-V(2)-O(14)#1	172.2(2)	O(8)-V(4)-O(5)#1	154.3(2)
O(10)-V(1)-O(12)	97.3(2)	O(4)-V(2)-O(14)#1	82.74(19)	O(2)-V(4)-O(10)	96.5(2)
O(11)-V(1)-O(12)	97.1(2)	O(5)-V(2)-O(14)#1	80.63(19)	O(6)-V(4)-O(10)	157.5(2)
O(10)-V(1)-O(13)	97.5(2)	O(13)-V(2)-O(14)#1	75.95(17)	O(8)-V(4)-O(10)	83.4(2)
O(11)-V(1)-O(13)	97.1(2)	O(12)#1-V(2)-O(14)#1	74.87(17)	O(5)#1-V(4)-O(10)	82.7(2)
O(12)-V(1)-O(13)	155.6(2)	O(3)-V(3)-O(9)	104.4(3)	O(2)-V(4)-O(14)	170.6(2)
O(10)-V(1)-O(14)	87.6(2)	O(3)-V(3)-O(8)	103.0(2)	O(6)-V(4)-O(14)	83.5(2)
O(11)-V(1)-O(14)	165.9(2)	O(9)-V(3)-O(8)	96.1(2)	O(8)-V(4)-O(14)	78.41(18)
O(12)-V(1)-O(14)	80.63(18)	O(3)-V(3)-O(12)#1	99.6(2)	O(5)#1-V(4)-O(14)	77.08(18)
O(13)-V(1)-O(14)	80.83(18)	O(9)-V(3)-O(12)#1	90.2(2)	O(10)-V(4)-O(14)	74.12(17)
O(10)-V(1)-O(14)#1	165.8(2)	O(8)-V(3)-O(12)#1	154.1(2)	O(1)-V(5)-O(6)#1	105.0(3)
O(11)-V(1)-O(14)#1	87.7(2)	O(3)-V(3)-O(13)	98.3(2)	O(1)-V(5)-O(4)	103.7(3)
O(12)-V(1)-O(14)#1	80.65(18)	O(9)-V(3)-O(13)	155.0(2)	O(6)#1-V(5)-O(4)	90.3(2)
O(13)-V(1)-O(14)#1	80.19(18)	O(8)-V(3)-O(13)	88.8(2)	O(1)-V(5)-O(9)#1	101.6(3)
O(14)-V(1)-O(14)#1	78.21(18)	O(12)#1-V(3)-O(13)	75.66(18)	O(6)#1-V(5)-O(9)#1	91.0(2)
O(7)-V(2)-O(4)	103.8(2)	O(3)-V(3)-O(14)	172.5(2)	O(4)-V(5)-O(9)#1	153.4(2)
O(7)-V(2)-O(5)	102.7(2)	O(9)-V(3)-O(14)	81.7(2)	O(1)-V(5)-O(11)	100.5(2)
O(4)-V(2)-O(5)	95.7(2)	O(8)-V(3)-O(14)	80.50(19)	O(6)#1-V(5)-O(11)	154.5(2)
O(7)-V(2)-O(13)	99.3(2)	O(12)#1-V(3)-O(14)	75.58(17)	O(4)-V(5)-O(11)	84.0(2)
O(4)-V(2)-O(13)	91.7(2)	O(13)-V(3)-O(14)	74.96(17)	O(9)#1-V(5)-O(11)	83.5(2)
O(5)-V(2)-O(13)	154.3(2)	O(2)-V(4)-O(6)	105.9(3)	O(1)-V(5)-O(14)#1	174.1(2)
O(7)-V(2)-O(12)#1	98.0(2)	O(2)-V(4)-O(8)	101.1(3)	O(6)#1-V(5)-O(14)#1	80.82(19)
O(4)-V(2)-O(12)#1	156.2(2)	O(6)-V(4)-O(8)	93.4(2)	O(4)-V(5)-O(14)#1	77.00(18)
O(5)-V(2)-O(12)#1	88.7(2)	O(2)-V(4)-O(5)#1	101.9(3)	O(9)#1-V(5)-O(14)#1	77.01(18)
O(13)-V(2)-O(12)#1	75.19(18)	O(6)-V(4)-O(5)#1	91.2(2)	O(11)-V(5)-O(14)#1	73.73(17)

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

Table 3 Selected Bond Lengths(nm) and Bond Angles(°) of Compound 2*

V(1)-O(13)	0.16872(11)	V(2)-O(2)#1	0.20860(14)	V(4)-O(7)	0.18886(17)
V(1)-O(12)	0.16979(14)	V(2)-O(4)	0.22956(15)	V(4)-O(5)	0.19287(16)
V(1)-O(1)	0.19256(15)	V(3)-O(6)	0.16571(18)	V(4)-O(13)#1	0.21013(13)
V(1)-O(2)	0.19339(16)	V(3)-O(8)	0.17865(16)	V(4)-O(4)	0.23099(11)
V(1)-O(4)	0.21292(11)	V(3)-O(5)	0.18191(12)	V(5)-O(9)	0.16358(18)
V(1)-O(4)#1	0.21341(13)	V(3)-O(2)	0.20022(12)	V(5)-O(11)	0.18803(15)
V(2)-O(3)	0.16131(18)	V(3)-O(1)#1	0.20905(13)	V(5)-O(8)	0.19286(18)
V(2)-O(14)	0.17867(15)	V(3)-O(4)	0.22450(15)	V(5)-O(14)	0.19292(18)
V(2)-O(7)	0.18425(14)	V(4)-O(10)	0.16154(15)	V(5)-O(12)	0.20562(11)
V(2)-O(1)	0.20028(10)	V(4)-O(11)	0.18018(17)	V(5)-O(4)	0.23742(13)
O(13)-V(1)-O(12)	106.86(7)	O(3)-V(2)-O(4)	170.44(6)	O(7)-V(4)-O(5)	153.80(5)
O(13)-V(1)-O(1)	97.34(7)	O(14)-V(2)-O(4)	82.06(7)	O(10)-V(4)-O(13)#1	95.94(7)
O(12)-V(1)-O(1)	96.98(7)	O(7)-V(2)-O(4)	79.55(6)	O(11)-V(4)-O(13)#1	157.53(5)
O(13)-V(1)-O(2)	97.52(6)	O(1)-V(2)-O(4)	75.03(5)	O(7)-V(4)-O(13)#1	83.01(6)
O(12)-V(1)-O(2)	97.39(7)	O(2)#1-V(2)-O(4)	73.82(5)	O(5)-V(4)-O(13)#1	82.17(6)
O(1)-V(1)-O(2)	155.34(6)	O(6)-V(3)-O(8)	104.29(8)	O(10)-V(4)-O(4)	169.71(7)
O(13)-V(1)-O(4)	165.35(6)	O(6)-V(3)-O(5)	102.28(8)	O(11)-V(4)-O(4)	83.81(5)
O(12)-V(1)-O(4)	87.79(5)	O(8)-V(3)-O(5)	96.66(6)	O(7)-V(4)-O(4)	78.28(5)
O(1)-V(1)-O(4)	80.62(5)	O(6)-V(3)-O(2)	99.28(6)	O(5)-V(4)-O(4)	76.90(5)
O(2)-V(1)-O(4)	80.02(5)	O(8)-V(3)-O(2)	92.24(6)	O(13)#1-V(4)-O(4)	73.78(5)
O(13)-V(1)-O(4)#1	87.12(6)	O(5)-V(3)-O(2)	153.80(7)	O(9)-V(5)-O(11)	105.28(7)
O(12)-V(1)-O(4)#1	166.02(5)	O(6)-V(3)-O(1)#1	96.98(7)	O(9)-V(5)-O(14)	101.05(9)
O(1)-V(1)-O(4)#1	80.57(6)	O(8)-V(3)-O(1)#1	156.65(7)	O(11)-V(5)-O(14)	91.12(7)
O(2)-V(1)-O(4)#1	80.64(6)	O(5)-V(3)-O(1)#1	88.00(5)	O(9)-V(5)-O(8)	103.83(8)
O(4)-V(1)-O(4)#1	78.23(4)	O(2)-V(3)-O(1)#1	74.70(5)	O(11)-V(5)-O(8)	90.09(7)
O(3)-V(2)-O(14)	106.64(8)	O(6)-V(3)-O(4)	171.05(6)	O(14)-V(5)-O(8)	153.83(6)
O(3)-V(2)-O(7)	102.88(7)	O(8)-V(3)-O(4)	83.56(6)	O(9)-V(5)-O(12)	100.53(7)
O(14)-V(2)-O(7)	96.77(6)	O(5)-V(3)-O(4)	80.74(6)	O(11)-V(5)-O(12)	154.18(6)
O(3)-V(2)-O(1)	100.42(7)	O(2)-V(3)-O(4)	75.82(5)	O(14)-V(5)-O(12)	83.37(6)
O(14)-V(2)-O(1)	91.17(6)	O(1)#1-V(3)-O(4)	74.59(5)	O(8)-V(5)-O(12)	84.23(6)
O(7)-V(2)-O(1)	152.01(7)	O(10)-V(4)-O(11)	106.46(7)	O(9)-V(5)-O(4)	174.15(7)
O(3)-V(2)-O(2)#1	96.96(7)	O(10)-V(4)-O(7)	101.12(8)	O(11)-V(5)-O(4)	80.40(5)
O(14)-V(2)-O(2)#1	154.46(7)	O(11)-V(4)-O(7)	94.05(8)	O(14)-V(5)-O(4)	77.21(6)
O(7)-V(2)-O(2)#1	87.15(6)	O(10)-V(4)-O(5)	101.80(8)	O(8)-V(5)-O(4)	77.22(6)
O(1)-V(2)-O(2)#1	74.79(5)	O(11)-V(4)-O(5)	91.47(7)	O(12)-V(5)-O(4)	73.78(5)

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

* V(2) and V(3) may be randomly replaced by Mo.

Table 4 Bond Valence Calculation of Selective O Atoms of Compound 1

atom	$\sum s_i$	atom	$\sum s_i$	atom	$\sum s_i$
μ_2 -O4	1.6998	μ_2 -O8	1.6776	μ_2 -O11	1.8124
μ_2 -O5	1.6352	μ_2 -O9	1.6599	μ_3 -O12	1.7390
μ_2 -O6	1.7338	μ_2 -O10	1.7933	μ_3 -O13	1.7598

Table 5 Bond Valence Calculation of Selective O Atoms of Compound 2

atom	$\sum s_i$	atom	$\sum s_i$	atom	$\sum s_i$
μ_2 -O5	1.6087	μ_2 -O11	1.7502	μ_2 -O14	1.6963
μ_2 -O7	1.6263	μ_2 -O12	1.8072	μ_3 -O1	1.7094
μ_2 -O8	1.6992	μ_2 -O13	1.7998	μ_3 -O2	1.7021

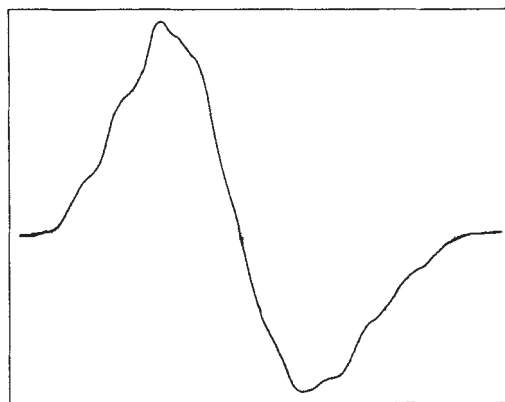


Fig. 2 EPR spectrum graphic of compound 2

green color of **2** is agreeable to the V^{IV} existence. The results of the empirical bond length/bond number calculation (the bond number valence of $V(5)$ is about 4.5) indicates one electron is reduced in the decavanadate anion of **2**. Based on the above analyses, the anion of **2** is formulated as $[Mo^{VI}V^{IV}V_8^{V}O_{28}]$.

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