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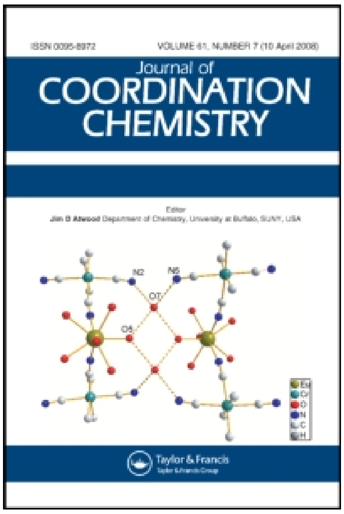

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Syntheses, spectroscopic characterization, thermal behavior, electrochemistry and crystal structures of two novel pyridine metatungstates

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SYNTHESES, SPECTROSCOPIC CHARACTERIZATION, THERMAL BEHAVIOR, ELECTROCHEMISTRY AND CRYSTAL STRUCTURES OF TWO NOVEL PYRIDINE METATUNGSTATES

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Two novel metatungstate compounds $[Hdmpy]_4H_2[H_2W_{12}O_{40}] \cdot 4H_2O$ (dmpy = 2,6-dimethyl pyridine) (**1**) and $[Hpy]_4H_2[H_2W_{12}O_{40}]$ (py = pyridine) (**2**) have been synthesized by rational reaction, rather than hydrothermal or electrosynthetic reaction, of sodium tungstate dihydrate with 2,6-dimethyl pyridine and pyridine, respectively and characterized by IR and electronic spectroscopies, thermal behavior and electrochemistry. X-ray single-crystal structural analyses indicate that both structures consist of close-packed arrangements of the almost spherical Keggin-type anion $[H_2W_{12}O_{40}]^{6-}$ with protonated 2,6-dimethyl pyridine or pyridine molecules filling the gap of the polyanions and interacting with the metatungstate anions in the mode of W-O···H-N or W-O···H-C, giving a two-dimensional network structure. The TG-DTA curves of **1** show that weight loss is divided into two stages, and reveal that the framework of the polyanion in **1** begins to decompose at 613°C. Electrochemical study shows that Compound **1** exhibits two chemically quasi-reversible one-electron reduction processes in aqueous solution (0.5 M NaCl + HCl) in the pH range 4–7.

Keywords: Metatungstate; Pyridine; Crystal structure; Synthesis

INTRODUCTION

The chemistry of polyoxometalate (POM) anions, an important subarea of modern inorganic chemistry, is dominated by tungsten and molybdenum in their +6 oxidation state [1]. Since the mid-1980s, these compounds have received increasing attention because of their interesting properties, importance as reagents in analytical procedures and wide applications in catalysis, biology, materials science and medicine as inorganic drugs [1–4]. In addition, POMs may be versatile inorganic building blocks for the construction of molecular-based materials. Before 1980, chemists realized that the anion of metatungstate, which was formulated as $[H_2W_{12}O_{40}]^{6-}$ according to previous NMR studies [5], was similar to heteropolyanions $[XW_{12}O_{40}]^{n-}$ with the Keggin-type

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structure (X = P, Si, Ge) [6–11]. However, the similarity between them could not be supported by reliable experimental data. In 1980, Jeannin *et al.* confirmed for the first time with a complete crystallographic study that the $H_8[H_2W_{12}O_{40}]^{4-}$ ion retained the original Keggin structure of the parent oxidized form [12]. The structure with three hydrogen atoms per cluster $[H_3W_{12}O_{40}]^{5-}$ was also investigated [9]. In 1996, Zavalij *et al.* reported a systematic investigation of the hydrothermal interaction of tungstic acid with methyl substituted ammonium cations, finding that the nature of the cations present in solution (the "templating ion") had a dramatic effect on the crystal structure of the phase formed, as does the pH, the temperature of the reaction medium and the transition metal [13]. In 2001, Boskovic *et al.* reported the electrosynthesis and solution structure of the six-electron reduced form of metatungstate $[H_2W_{12}O_{40}]^{6-}$ [14]. The crystal structure of unreduced $[H_2W_{12}O_{40}]^{6-}$ has not been reported. In this paper, we report the syntheses, spectroscopic characterization, thermal behavior, electrochemistry and X-ray crystal structures of the title Compounds **1** and **2** which contain the unreduced $[H_2W_{12}O_{40}]^{6-}$ anion. In addition, through bond-valence parameters obtained from a systematic analysis [15], we also surmise that two protons reside in the tetrahedral cavity of the metatungstate anion.

EXPERIMENTAL

Physical Measurements and Materials

All chemicals used for syntheses were reagent grade and used without further purification.

C, H, N elemental analyses were performed on a Perkin-Elmer 240C instrument. The IR spectra were measured as KBr discs in the range 4000–400 cm^{-1} using a Nicolet 170 SXFT-IR spectrophotometer. Electronic spectra were obtained on a Shimadzu UV-250 spectrophotometer between 400 and 190 nm (in water). Thermogravimetric analysis was carried out under air on a Perkin-Elmer-7 thermal analyzer at a heating rate of 10°C/min from 18 to 900°C. Electrochemical measurements were performed on an LK98 microcomputer-based electrochemical system (LANLIKE, Tianjin, China). A three-electrode system was employed for cyclic voltammetry. A 4-mm diameter glassy carbon disk electrode (GCE) (homemade) was used as a working electrode, a platinum wire served as the counter electrode and an Ag/AgCl electrode as the reference electrode. The glassy carbon electrode was polished before each experiment with 1-µm α-alumina powder, rinsed thoroughly with doubly distilled water between each polishing step, sonicated successively in 1:1 nitric acid, acetone and doubly distilled water and then allowed to dry at ambient temperature.

Preparations of Compounds

$[Hdmpy]_4H_2[H_2W_{12}O_{40}]\cdot 4H_2O$ (1)

A 1.5 g sample of commercial sodium tungstate dihydrate $Na_2WO_4\cdot 2H_2O$ was dissolved in 20 cm^3 distilled H_2O, and then 1 cm^3 2,6-dimethyl pyridine was added. The mixture was then acidified with 2 M HCl to the desired pH 5 with stirring, resulting in the formation of a white gel, which soon disappeared. The mixture was allowed to react for 3 h, then filtered and left to evaporate at room temperature. Several weeks later, good quality colorless crystals were obtained. Anal. Calcd. for $[Hdmpy]_4H_2[H_2W_{12}O_{40}] \cdot 4H_2O$(%): C, 10.02; H, 1.56; N, 1.67. Found: C, 10.13; H, 1.63; N, 1.51.

[Hpy]$_4$H$_2$[H$_2$W$_{12}$O$_{40}$] (2)

Compound **2** was synthesized in a manner analogous to that employed for synthesis of **1**, with pyridine used in place of 2,6-dimethyl pyridine and the pH set at 4.5. Colorless crystals were obtained. Anal. Calcd. for $[Hpy]_4H_2[H_2W_{12}O_{40}]$(%): C, 7.58; H, 0.89; N, 1.77. Found: C, 7.62; H, 0.94; N, 1.70.

X-ray Crystallography and Structure Solution

The crystal structures of Compounds **1** and **2** were determined from single-crystal X-ray diffraction data. The intensity data were collected with a Rigaku RAXIS-IV image plate area detector using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using 97 [16] to $R1 = 0.0579$ ($wR2 = 0.1147$) for **1** for 11057 independent reflections [$I > 2\sigma(I)$] of 11057 reflections collected in the range $2.13 < \theta < 24.60°$ and $R1 = 0.0634$ ($wR2 = 0.1310$) for **2** for 7853 independent reflections [$I > 2\sigma(I)$] of 13200 reflections collected in the range $1.13 < \theta < 25.00°$, respectively. The intensity data were corrected for Lorentz and polarization effects as well as for empirical absorption. All nonhydrogen atoms were refined anisotropically, and the hydrogen atoms, except in water molecules, were placed in calculated positions. The hydrogen atoms in water molecules were located from the difference Fourier map. The final electron density difference maps showed maxima and minima ranging from 3.309 and -2.681 eÅ^{-3} for **1**, 2.559 and -1.846 e Å^{-3} for **2**. Crystal and data collection parameters along with the values for the residuals after final refinement are summarized in Table I.

RESULTS AND DISCUSSION

Crystal Structures of 1 and 2

The two compounds $[Hdmpy]_4H_2[H_2W_{12}O_{40}] \cdot 4H_2O$ and $[Hpy]_4H_2[H_2W_{12}O_{40}]$ were prepared by rational reactions. Molecular structure representations of Compounds **1** and **2** with the labeling scheme are shown in Figs. 1 and 2, respectively. The polyhedral representation of the anion is presented in Fig. 3. The two-dimensional network structure arrangement of Compound **1** is given in Fig. 4. Selected bond lengths and angles for Compounds **1** and **2** are listed in Tables II and III, respectively.

The molecular structure of **1** consists of four discrete protonated 2,6-dimethyl pyridine molecules, two H^+ cations, four crystal water molecules and a $[H_2W_{12}O_{40}]^{6-}$ anion, which has an effective C_{3v} point symmetry. The dodecatungstate cluster of the title compounds exists in its most common α form, which can be described as a cubo-octahedral framework of tungsten atoms. The oxygen atoms [O(37), O(38), O(39), O(40)] form an almost close-packed structure with a tetrahedral cavity inside the cluster, which is occupied by two disordered H atoms based on bond valence

TABLE I Summary of crystal data and refinement results for Compounds **1** and **2**

	1	**2**
Formula	$C_{28}H_{52}N_4O_{44}W_{12}$	$C_{20}H_{28}N_4O_{40}W_{12}$
Formula weight	3354.93	3170.66
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	12.616(3)	18.210(4)
b (Å)	14.120(3)	19.713(4)
c (Å)	22.623(5)	15.069(3)
α (°)	86.32(3)	90
β (°)	79.58(3)	97.68(3)
γ (°)	66.99(3)	90
Volume (Å^3)	3648.0(13)	5360.8(18)
Z	2	4
Density (calculated) (g cm^{-3})	3.051	3.929
Absorption coefficient (mm^{-1})	18.918	25.729
F(000)	2968	5536
Crystal size (mm)	0.26 × 0.13 × 0.11	0.21 × 0.10 × 0.08
Θ range for data collection (°)	2.13 to 24.60	1.13 to 25.00
Limiting indices	$0 \le h \le 14$ $-14 \le k \le 16$ $-26 \le l \le 26$	$-21 \le h \le 21$ $-23 \le k \le 23$ $0 \le l \le 17$
Reflections collected	11057	13200
Independent reflections	11057	7853
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	11057/791/778	7853/0/686
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.2301 and 0.0838	0.2327 and 0.0745
Goodness-of-fit on F^2	0.765	1.126
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0579$ $wR2 = 0.1147$	$R1 = 0.0634$ $wR2 = 0.1310$
Largest difference peak and hole (e Å^{-3})	3.309 and −2.681	2.559 and −1.846

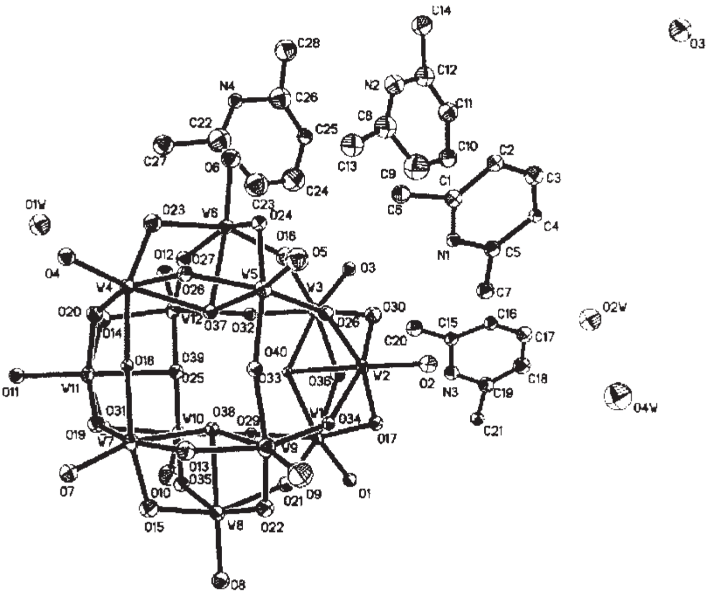

FIGURE 1 Molecular structure of Compound **1** with labeling scheme; thermal ellipsoids are drawn at the 30% probability level.

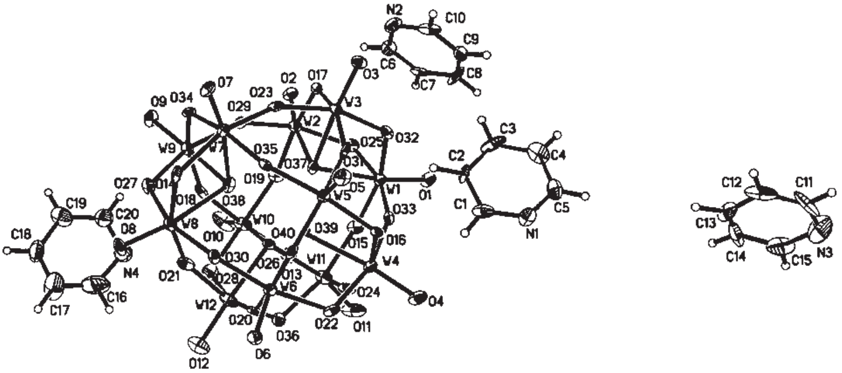

FIGURE 2 Molecular structure of Compound **2** with labeling scheme; thermal ellipsoids are drawn at the 30% probability level.

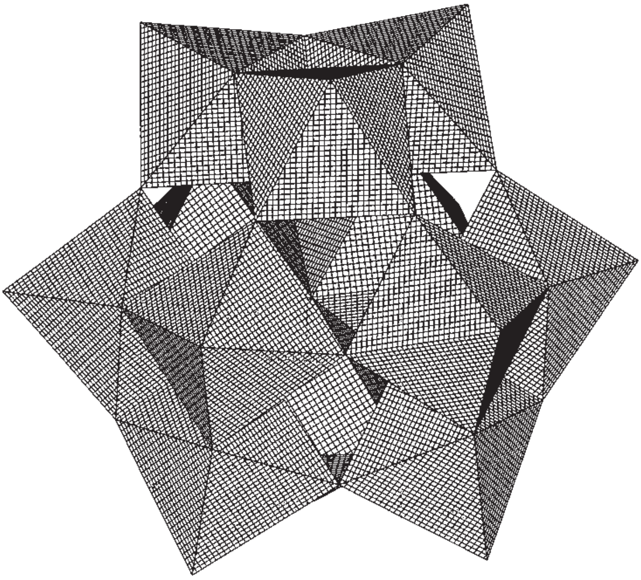

FIGURE 3 Polyhedral representation of the title anion.

sum calculations [15] and earlier NMR studies [5]. The anion of $[H_2W_{12}O_{40}]^{6-}$ exhibits the usual arrangement of four W_3O_{13} groups, each of them in association with three edge-sharing WO_6 octahedra. This structure is in good agreement with that previously reported [13]. Four kinds of oxygen atoms are present: the first, O_t, is double bonded with a tungsten atom. The second and third, O_b and O_c, bridge two tungsten atoms (O_b atoms are shared by two tungsten atoms from different W_3O_{13} units; O_c atoms are shared by two tungsten atoms from the same W_3O_{13} unit). The last, O_d, is linked to three tungsten octahedra in the range of the same W_3O_{13} group. Accordingly, they have different W–O distances. In the anion of Compound **1**, the W–O_t, W–$O_{b(c)}$ and W–O_d distances are in the range 1.68(4)–1.76(3), 1.76(3)–2.05(3) and 2.16(3)–2.33(3) Å, respectively. The shortest W–O_t distance agrees with the W–O double

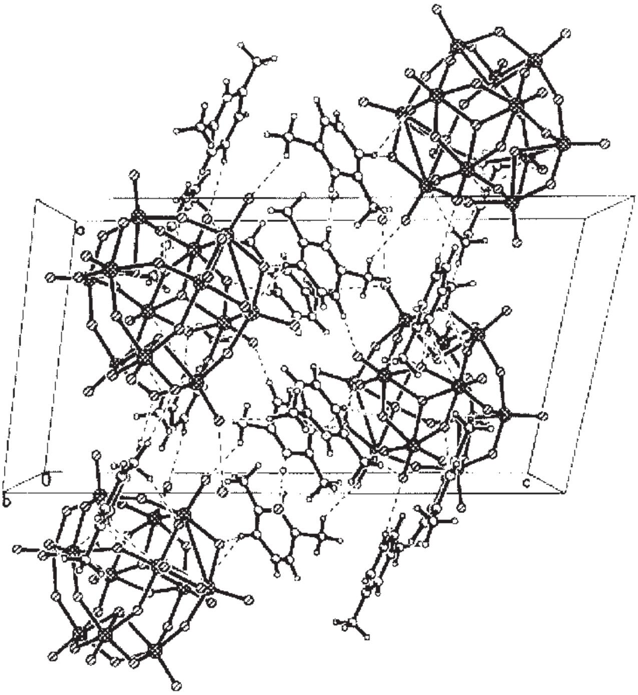

FIGURE 4 Two-dimensional network structure arrangement of Compound **1**.

bond length. These bond lengths are almost consistent with the previous reference [13]. The W–O$_d$ atoms form a tetrahedron inside the title anion. Two disordered H atoms occupy this empty tetrahedral cavity. The three ranges of W–O distances distribution are in good agreement with the results obtained from $\nu_{as}(W{=}O_t)$, $\nu_{as}(W{=}O_{b(c)})$ and $\nu_{as}(W{=}O_d)$ vibrations from IR absorption peaks.

Comparing the unreduced $[H_2W_{12}O_{40}]^{6-}$ anion (in this work) with the reduced $[H_2W_{12}O_{40}]^{12-}$ anion (in the previous paper [12]), the differences lie in the WO$_6$ octahedra. In the unreduced $[H_2W_{12}O_{40}]^{6}$ anion one kind of WO$_6$ octahedron exists [W–O$_t$, W–O$_{b(c)}$ and W–O$_d$ distances can be seen above for Compound **1**, and the W(11)–W(12) short distance is 3.226(3) Å in the same compound] whereas in the reduced $[H_2W_{12}O_{40}]^{12-}$ anion there are two kinds of WO$_6$ octahedra [$d_{W\text{–}Ot}$: 1.69(2), $d_{W\text{–}Ob(c)}$: 1.905(5)–1.97(2), $d_{W\text{–}Od}$: 2.32(2) Å, W–W short distance 3.312(7) Å] and WO$_6$ octahedra [$d_{W\text{–}Ot}$: 2.13(2), $d_{W\text{–}Ob(c)}$: 1.80(3)–2.04(1), $d_{W\text{–}Od}$: 1.88(2) Å, W–W short distance 2.50(2) Å) [12].

The presence of numerous heavy atoms in the structure precludes the determination of hydrogen atom positions. Although we cannot determine the sites of the H$^+$ ions of $[H_2W_{12}O_{40}]^{6-}$ from the X-ray structure, based on the band valence parameters [15], the bond valence sums for the O(37–40) atoms in the title anion of Compound **1** are determined by fitting Eq. (1):

$$V_i = \sum_j S_{ij} = \sum_j \exp\left(\frac{r'_o - r_{ij}}{B}\right). \tag{1}$$

TABLE II Selected bond lengths (Å) and bond angles (°) for Compound **1**

W(1)–O(1)	1.75(3)	W(2)–O(2)	1.70(3)
W(3)–O(3)	1.78(3)	W(4)–O(4)	1.73(3)
W(5)–O(5)	1.68(4)	W(6)–O(6)	1.78(3)
W(7)–O(7)	1.74(3)	W(8)–O(8)	1.72(3)
W(9)–O(9)	1.70(3)	W(10)–O(10)	1.72(4)
W(11)–O(11)	1.74(3)	W(12)–O(12)	1.76(3)
W(1)–O(21)	1.84(3)	W(1)–O(17)	1.93(3)
W(1)–O(29)	1.93(3)	W(1)–O(36)	1.98(3)
W(2)–O(26)	1.88(3)	W(2)–O(17)	1.94(3)
W(2)–O(30)	1.94(3)	W(2)–O(34)	1.95(3)
W(3)–O(32)	1.86(3)	W(3)–O(16)	1.98(3)
W(3)–O(36)	1.89(3)	W(3)–O(30)	1.96(3)
W(4)–O(18)	1.96(2)	W(4)–O(23)	1.82(3)
W(4)–O(20)	1.84(3)	W(4)–O(28)	1.93(3)
W(5)–O(28)	1.88(3)	W(5)–O(24)	1.92(3)
W(5)–O(26)	1.93(3)	W(5)–O(33)	1.93(3)
W(6)–O(16)	1.84(3)	W(6)–O(24)	1.88(3)
W(6)–O(27)	1.92(3)	W(6)–O(23)	2.05(3)
W(7)–O(13)	1.76(3)	W(7)–O(18)	1.84(2)
W(7)–O(15)	1.99(3)	W(7)–O(19)	2.04(3)
W(8)–O(15)	1.80(3)	W(8)–O(22)	1.88(3)
W(8)–O(35)	1.91(3)	W(8)–O(21)	2.00(3)
W(9)–O(22)	1.80(3)	W(9)–O(34)	1.87(3)
W(9)–O(33)	1.92(3)	W(5)–O(13)	1.92(3)
W(10)–O(29)	1.87(3)	W(5)–O(35)	1.91(3)
W(10)–O(25)	1.92(3)	W(10)–O(31)	1.95(3)
W(11)–O(19)	1.82(3)	W(11)–O(31)	1.94(3)
W(11)–O(14)	2.00(3)	W(11)–O(20)	2.00(3)
W(12)–O(14)	1.87(3)	W(12)–O(27)	1.87(3)
W(12)–O(25)	1.91(3)	W(12)–O(32)	1.97(3)
W(1)–O(40)	2.19(2)	W(2)–O(40)	2.25(3)
W(3)–O(40)	2.25(2)	W(4)–O(37)	2.23(3)
W(5)–O(37)	2.25(3)	W(6)–O(37)	2.33(3)
W(7)–O(38)	2.17(3)	W(8)–O(38)	2.21(2)
W(9)–O(38)	2.16(3)	W(10)–O(39)	2.16(3)
W(11)–O(39)	2.21(3)	W(12)–O(39)	2.16(3)
N(1)–C(1)	1.32(5)	N(1)–C(5)	1.37(5)
N(1)–H(1A)	0.8600	N(2)–C(8)	1.25(6)
N(2)–C(12)	1.41(7)	N(2)–H(2A)	0.8600
O(1)–W(1)–O(21)	103.5(12)	O(1)–W(1)–O(17)	98.6(13)
O(21)–W(1)–O(17)	91.2(13)	O(1)–W(1)–O(29)	99.6(12)
O(21)–W(1)–O(29)	87.9(12)	O(17)–W(1)–O(29)	161.5(11)
O(1)–W(1)–O(36)	94.8(12)	O(21)–W(1)–O(36)	161.7(11)
O(17)–W(1)–O(36)	87.3(12)	O(29)–W(1)–O(36)	87.8(12)
O(1)–W(1)–O(40)	168.5(11)	O(21)–W(1)–O(40)	87.0(10)
O(17)–W(1)–O(40)	76.0(10)	O(29)–W(1)–O(40)	85.5(10)
O(36)–W(1)–O(40)	75.0(10)	W(1)–O(40)–W(2)	94.5(10)
W(1)–O(40)–W(3)	94.6(10)	W(2)–O(40)–W(3)	94.3(9)

The summations of bond valences of O(37–40) atoms in the anion of Compound **1** are 1.16, 1.48, 1.49 and 1.29 for O(37) to O(40), respectively. These bond valence sums are far from 2, strongly suggesting that every O(37–40) atom should be combined with another atom. In addition, the title anion of **1** is considered to have a total charge of minus six based on charge balance considerations. This charge requires four protons, which are assumed to be bound directly to pyridine molecules, just as analysis of bond valence sum calculations for four O_d atoms allows the assignment of specific binding sites for these protons. For N(1), the summation of bond valences N(1)–C(5) (1.22)

TABLE III Selected bond lengths (Å) and bond angles (°) for Compound **2**

W(1)–O(1)	1.685(18)	W(2)–O(2)	1.710(17)
W(3)–O(3)	1.696(16)	W(4)–O(4)	1.71(2)
W(5)–O(5)	1.695(17)	W(6)–O(6)	1.716(16)
W(7)–O(7)	1.699(15)	W(8)–O(8)	1.710(16)
W(9)–O(9)	1.713(17)	W(10)–O(10)	1.668(19)
W(11)–O(3)	1.73(2)	W(12)–O(12)	1.712(18)
W(1)–O(15)	1.911(18)	W(1)–O(33)	1.923(19)
W(1)–O(25)	1.927(18)	W(1)–O(32)	1.902(15)
W(2)–O(25)	1.949(17)	W(2)–O(29)	1.877(16)
W(2)–O(19)	1.916(16)	W(2)–O(17)	1.922(15)
W(3)–O(32)	1.964(17)	W(3)–O(31)	1.871(16)
W(3)–O(23)	1.890(17)	W(3)–O(17)	1.939(16)
W(4)–O(22)	1.973(17)	W(4)–O(24)	1.901(19)
W(4)–O(33)	1.933(17)	W(4)–O(16)	1.942(17)
W(5)–O(35)	1.917(16)	W(5)–O(16)	1.931(17)
W(5)–O(31)	1.933(17)	W(5)–O(13)	1.968(15)
W(6)–O(13)	1.903(17)	W(6)–O(30)	1.914(17)
W(6)–O(20)	1.945(16)	W(6)–O(22)	1.949(17)
W(7)–O(35)	1.920(16)	W(7)–O(23)	1.923(17)
W(7)–O(34)	1.930(16)	W(7)–O(14)	1.936(16)
W(8)–O(21)	1.885(15)	W(8)–O(27)	1.894(17)
W(8)–O(14)	1.920(16)	W(8)–O(30)	1.929(17)
W(9)–O(18)	1.878(18)	W(9)–O(27)	1.931(16)
W(9)–O(34)	1.934(16)	W(9)–O(29)	1.955(16)
W(10)–O(26)	1.80(2)	W(10)–O(19)	1.921(16)
W(10)–O(28)	1.959(16)	W(10)–O(18)	1.963(19)
W(11)–O(15)	1.902(17)	W(11)–O(24)	1.93(2)
W(11)–O(26)	2.00(2)	W(1)–O(36)	2.014(14)
W(12)–O(36)	1.84(2)	W(12)–O(20)	1.877(18)
W(12)–O(21)	1.952(18)	W(12)–O(28)	1.999(19)
W(1)–O(37)	2.272(15)	W(2)–O(37)	2.280(15)
W(3)–O(37)	2.323(14)	W(4)–O(39)	2.240(14)
W(5)–O(39)	2.247(16)	W(6)–O(39)	2.224(14)
W(7)–O(38)	2.274(16)	W(8)–O(38)	2.256(16)
W(9)–O(38)	2.313 (16)	W(10)–O(40)	2.187(17)
W(11)–O(40)	2.234(15)	W(12)–O(40)	2.165(14)
O(1)–W(1)–O(25)	98.9(8)	O(32)–W(1)–O(25)	90.5(7)
O(15)–W(1)–O(25)	89.4(7)	O(33)–W(1)–O(25)	160.1(7)
O(1)–W(1)–O(37)	170.4(7)	O(32)–W(1)–O(37)	75.2(6)
O(15)–W(1)–O(37)	85.9(6)	O(33)–W(1)–O(37)	86.6(6)
O(25)–W(1)–O(37)	74.2(6)	O(2)–W(2)–O(29)	101.1(7)
O(2)–W(2)–O(19)	99.6(8)	O(29)–W(2)–O(19)	86.5(7)
O(2)–W(2)–O(17)	100.5(7)	O(29)–W(2)–O(17)	89.9(6)
O(19)–W(2)–O(17)	159.9(7)	O(2)–W(2)–O(25)	99.0(8)
O(29)–W(2)–O(25)	159.7(7)	O(19)–W(2)–O(25)	87.7(7)
O(17)–W(2)–O(25)	88.9(6)	O(2)–W(2)–O(37)	170.6(7)
O(29)–W(2)–O(37)	86.6(6)	O(19)–W(2)–O(37)	86.2(6)
O(17)–W(2)–O(37)	73.8(6)	O(25)–W(2)–O(37)	73.7(6)
W(1)–O(37)–W(2)	93.8(5)	W(1)–O(37)–W(3)	92.9(5)
W(2)–O(37)–W(3)	93.4(5)	W(8)–O(38)–W(7)	94.3(6)
W(8)–O(38)–W(9)	93.3(6)	W(7)–O(38)–W(9)	93.5(6)
W(6)–O(39)–W(4)	95.8(5)	W(6)–O(39)–W(5)	94.4(6)
W(4)–O(39)–W(5)	94.3(6)	W(12)–O(40)–W(10)	98.5(7)
W(12)–O(40)–W(11)	97.4(6)	W(10)–O(40)–W(11)	95.5(6)

and N(1)–C(1) (1.39) leads to a value of 2.61, which is far from 3, strongly suggesting monoprotonation. Similarly, the summations of bond valences of N(2), N(3), and N(4) are 2.77, 2.18, and 2.22, respectively.

It should be noted that the protonated 2,6-dimethyl pyridine and crystal water molecules fill the gap of the polyanions, and interact with the metatungstate anions by either W–O···H–N or W–O···H–C forces, owing to $d_{N\text{–}H\cdots O}$ in the range of 2.737–2.922 Å and $d_{C\text{–}H\cdots O}$ varying from 3.339 to 3.521 Å, which gives the infinite two-dimensional network structure. Therefore, the interactions between the organic charge compensation cations and the polyanions are mainly hydrogen bonds, van der Waals and electrostatic forces.

The structure of **2** is similar to that of **1** with pyridine in place of 2,6-dimethyl pyridine. The crystal structure of **2** is composed of four discrete protonated pyridine molecules, two H^+ cations, and one $[H_2W_{12}O_{40}]^{6-}$ anion. In the anion of **2**, the W–O_t, W–$O_{b(c)}$ and W–O_d distances are in the range 1.668(19)–1.73(2), 1.80(2)–1.999(19) and 2.165(14)–2.323(14) Å, respectively. The shortest W–O_t distances and the longest W–O_d distances are approximately the same as those of **1**. The bond orders for O(37–40) atoms in the anion of Compound **2** are 1.22, 1.25, 1.41 and 1.58 for O(37) to O(40), respectively. This also indicates that every two O(37–40) atoms are connected with an H^+ ion, which is indicative of the presence of having two H^+ ions in the empty cavity of anion **2**.

FTIR Spectra

In the FTIR spectra of **1** and **2**, there are four characteristic asymmetric vibrations resulting from a heteropolyanion with the Keggin-type structure, namely, $\nu_{as}(W{=}O_t)$, $\nu_{as}(W\text{–}O_b)$, $\nu_{as}(W\text{–}O_c)$ and $\nu_{as}(W{=}O_d)$. The peaks appear at 932, 878, 767 and 832 cm^{-1}, respectively, for **1** and 934, 880, 766 and 832 cm^{-1} for **2**. Comparing the FTIR spectra of Compounds **1** and **2** with those of $[Bu_4N]_5H[H_2W_{12}O_{40}]$ [14], the W–O_b band appears at a nearly identical frequency; the W=O_t and W–O_c bond vibrations have different red-shifts. In addition, the resonances at 3082 and 1402 cm^{-1} in **1** and **2** were assigned to the ν_{as}(C–H of aryl groups) and ν_{as}(C–N of aryl groups) stretching vibrations of 2,6-dimethyl pyridine and pyridine molecules. The FTIR spectral studies indicate that there is strong interaction between the polyanions and organic groups mainly by electrostatic forces and hydrogen bonds in the solid state.

Electronic Spectra

The electronic spectra of **1** and **2** in aqueous solution are very similar. The two absorption peaks, appearing at ca. 190 and 260 nm in the UV region are observed in the electronic spectra of the title compounds, which are assigned to the $p\pi \rightarrow d\pi$ charge-transfer absorption of $O_t \rightarrow W$ and $O_{b(c)} \rightarrow W$, respectively. The latter is the characteristic absorption peak of the heteropolyanion, which is not affected by anion protonation; but the former is affected by the different electrolyte in solution.

Voltammetric Behavior

Figure 5 shows cyclic voltammograms of 1 mM $[Hdmpy]_4H_2[H_2W_{12}O_{40}]\cdot 4H_2O$ in aqueous solution (0.5 M NaCl + HCl), where the metatungstate anion exhibits a

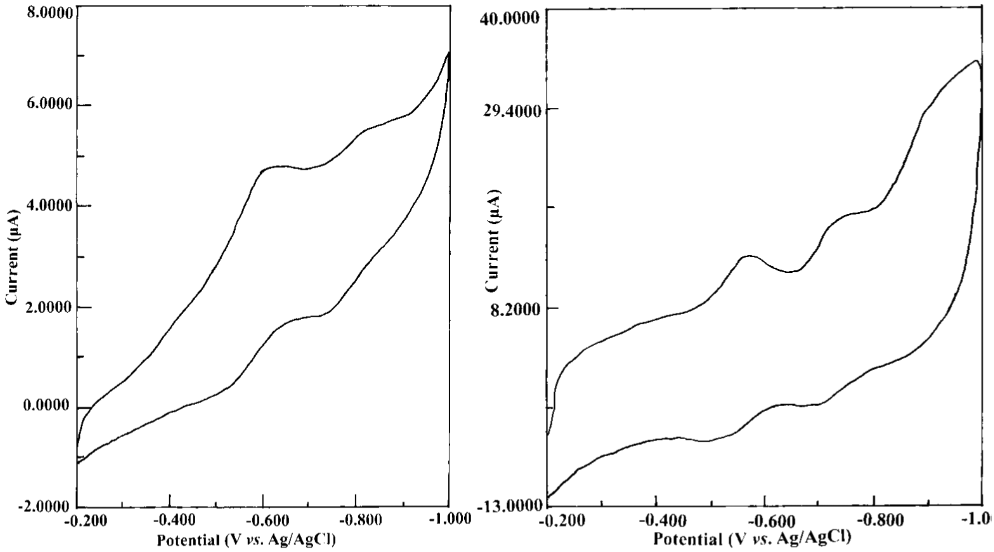

FIGURE 5 Cyclic voltammograms of a 1 mM solution of Compound **1** at pH 6.72 (left) pH 4.64 (right) in aqueous solution containing 0.5 M NaCl + HCl.

kinetically stable and reproducible voltammetric pattern, at least in the pH 6.72 and pH 4.64 media studied here. At pH 6.72, one comparatively well-defined redox wave, which involved a one-electron transfer, appeared with midpoint potential (E_{mid}) of −0.576 V, followed by an ill-defined wave, which also corresponded to a one-electron process with midpoint potential of −0.781 V, where $E_{\mathrm{mid}} = (E_{\mathrm{pc}} + E_{\mathrm{pa}})/2$; E_{pc} and E_{pa} are cathodic and anodic peak potentials. The one-electron wave is chemically quasi-reversible because the E_{pc} and E_{pa} values are not dependent on the voltage scan rate (1–100 $\mathrm{mV\,s^{-1}}$), and the peak-potential separation is approximately unchanged at ca. 83 mV. In the pH 4.64 medium, relative to the values observed in the pH 6.72 solution, shifts of the two peak potentials by 56 mV for the first redox wave and 64 mV for the second in the positive direction were observed. Under these conditions, the metatungstate anion exhibits two nearly reversible one-electron reduction processes with peak-potential separation of 60 mV for the first redox wave and 69 mV for the second. These results are in good agreement with the previous analysis [17].

Thermal Behavior Analysis

The TG-DTA study of **1** shows two stages of weight loss (as shown in Fig. 6). The first weight loss of 2.73% occurs between 18 and 187.0°C, corresponding to the loss of four crystal water molecules. The second weight loss of 13.25% happens between 187.0 and 820.1°C. Two exothermic peaks at 417.0 and 613.8°C in the DTA curve are ascribed to the loss of organic groups and structural water molecules. The experimental value of the gross weight loss of 15.98% is in approximate accord with the calculated value of 17.06%. It should be noted that the exothermic peak appearing at 613.8°C in the DTA curve indicates the destruction of the backbone structure of the metatungstate anion.

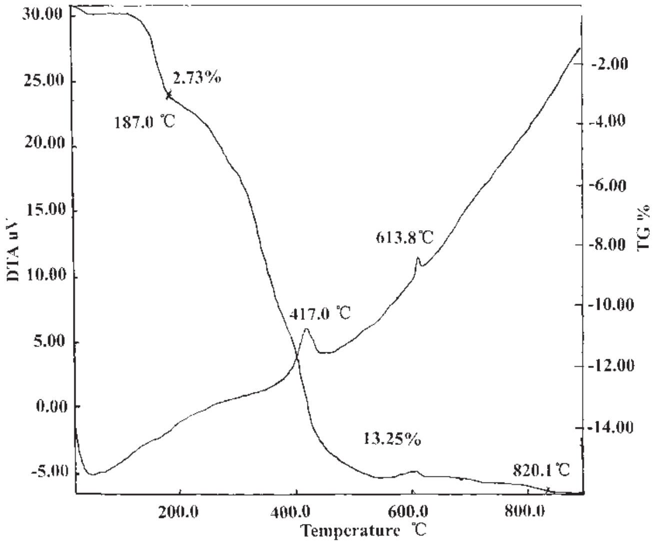

FIGURE 6 The TG-DTA curves of Compound **1**.

CONCLUSIONS

Two novel pyridine compounds containing metatungstate building blocks have been synthesized by rational reaction, structurally characterized and investigated by thermal behavior and electrochemistry. From our investigation, we suggest that these two compounds may attract great interest in applications such as catalysis and electronic materials.

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Supplementary Data

Crystallographic data for the structural analyses reported in this paper have been deposited with the Cambridge Crystallographic Data Centre with CCDC numbers 217170 for **1** and 217171 for **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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