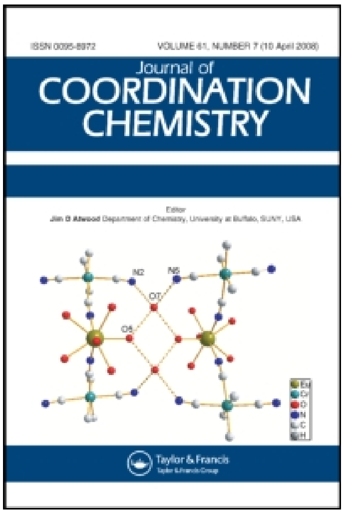

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An organic-inorganic hybrid polyoxometalate based on the dodecatungstate building block: $[Ni(phen)(H_2O)_3]_2[Ni(H_2O)_5][H_2W_{12}O_{40}] \cdot 6H_2O$

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An organic-inorganic hybrid polyoxometalate $[Ni(phen)(H_2O)_3]_2[Ni(H_2O)_5][H_2W_{12}O_{40}] \cdot 6H_2O$ (phen = 1,10-phenanthroline) has been isolated and characterized by IR, UV, electrochemistry and single-crystal X-ray diffraction. X-ray crystallographic study indicates that the title compound is monoclinic, space group $C2/c$, with lattice constants $a = 21.7672(17)$, $b = 16.1189(12)$, $c = 20.7949(16)$ Å, $\beta = 107.8440(10)^\circ$, $V = 6945.2(9)$ Å^3, $D_c = 3.528\ \mathrm{Mg\,m^{-3}}$, $F(000) = 6600$, $Z = 4$, $R_1 = 0.0372$, $wR_2 = 0.0845$. The molecular fragment of the title compound consists of two supporting $[Ni(phen)(H_2O)_3]^{2+}$ coordination cations, one supporting $[Ni(H_2O)_5]^{2+}$ unit, one metatungstate polyoxoanion $[H_2W_{12}O_{40}]^{6-}$ and six H_2O molecules of crystallization.

Keywords: Dodecatungstate; Polyoxometalate; Nickel ion

1. Introduction

Polyoxometalates (POMs), as early transition metal oxide clusters, constitute a large family of compounds bearing surprising electronic versatility and structural diversity, endowing them with applications in fields such as catalysis, material science, medicine, and photochemistry. [1–5] Hybrid organic-inorganic polyoxometalate derivatives have attracted interest due to unusual structures, properties and applications [6]. To date, many hybrid compounds containing vanadium [7] and molybdenum [8] isopolyoxoanions have been reported; functionalization of dodecatungstate isopolyoxoanions as building units have not been so extensively studied, and development and exploration of the functionalization of the dodecatungstate as building units for the systematic modification of POM systems remains a challenge. Currently, we are investigating the system of dodecatungstate and transition-metal-phen compounds in search of the preparation of new hybrid compounds. In this article, we report the

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synthesis, crystal structure and electrochemical properties of $[Ni(phen)(H_2O)_3]_2[Ni(H_2O)_5][H_2W_{12}O_{40}] \cdot 6H_2O$.

2. Experimental

All chemicals purchased were of reagent grade and used without further purification.

2.1. *Synthesis of* $[Ni(phen)(H_2O)_3]_2[Ni(H_2O)_5][H_2W_{12}O_{40}] \cdot 6H_2O$

The title compound $[Ni(phen)(H_2O)_3]_2[Ni(H_2O)_5][H_2W_{12}O_{40}] \cdot 6H_2O$ was synthesized by conventional aqueous solution method. A solution of 1.98 g (6.0 mmol) $Na_2WO_4 \cdot 2H_2O$ in 20 mL distilled water was acidified using 4 mol L^{-1} HCl to pH 4.80 under stirring at room temperature, and then 0.1 g (0.5 mmol) phen and 1.0 g (4.2 mmol) $NiCl_2 \cdot 6H_2O$ were added successively. The resulting solution was refluxed for 3 h and filtered. Slow evaporation of the filtrate at ambient temperature after a few days results in good quality green crystals suitable for X-ray diffraction. Crystallization of the title compound was highly sensitive to the pH value of the starting mixture. Anal. Calcd (%): Ni, 4.77; W, 59.77; found: (%) Ni, 4.65; W, 59.69; IR (KBr pellet, cm^{-1}): 1651(s), 1634(s), 1429(m), 1403(m), 1362(w), 1004(w), 932(m), 886(m), 831(s), 763(w), 697(m), 671(m) cm^{-1}.

2.2. *Crystal data collection and structure determination*

A green single crystal of the title compound (0.14 mm × 0.10 mm × 0.09 mm) was mounted on a glass fiber capillary. The data were collected on a Rigaku RAXIS-IV diffractometer with Mo-Kα ($\lambda = 0.71073$ Å) at 292(2) K in the range of $1.73 < \theta < 25.00°$. A total of 16519 (5930 unique, $R_{\text{int}} = 0.0398$) reflections were measured ($-25 \leq h \leq 22$, $-13 \leq k \leq 19$, $-24 \leq l \leq 24$). Direct methods were used to solve the structure and to locate the heavy atoms (SHELXS97). The remaining atoms were found from successive difference maps (SHELXL97). The structure was refined by the full-matrix least-squares method on F^2 as well as empirical absorption correction and routine Lorentz and polarization corrections using the SHELXL-97 software [9]. All non-hydrogen atoms were refined anisotropically. A summary of crystal data, and structure refinement for the title compound is provided in table 1; selected bond lengths and hydrogen bonds are listed in tables 2 and 3, respectively.

2.3. *Physical measurements*

Infra red (IR) spectrum was recorded on a Nicolet 170 FT infrared spectrophotometer with a sample prepared as a KBr pellet in the range of 4000–400 cm^{-1}. UV spectrum was obtained on a Unican UV-500 spectrometer (distilled water as solvent) in the range 400–190 nm (in water). Inductively coupled plasma (ICP) analyses were carried out on Jarrel-Ash J-A1100 spectrometer. 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

Table 1. Crystal data collection and refinement for the title compound.

Formula	$C_{24}H_{52}N_4Ni_3O_{57}W_{12}$
Fw	3691.01
Temperature (K)	292(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å, °)	
a	21.7672(17)
b	16.1189(12)
c	20.7949(16)
β	107.8440(10)
Volume (Å^3)	6945.2(9)
Z	4
Density (calculated) (Mg m^{-3})	3.528
Absorption coefficient (mm^{-1})	20.685
$F(000)$	6600
Crystal size (mm^3)	$0.14 \times 0.10 \times 0.09$
θ range for data collection (°)	1.73 to 25.00
Limiting indices	$-25 \leq h \leq 22$, $-13 \leq k \leq 19$, $-24 \leq l \leq 24$
Reflections collected	16519
Independent reflections	5930 ($R_{\text{int}} = 0.0398$)
Completeness to $\theta = 25.00°$	97.0%
Data/restraints/parameters	5930/18/497
GOF	1.085
Final R indices [$I > 2(I)$]	$R_1 = 0.0372$, $wR_2 = 0.0845$
Largest diffraction peak and hole (e Å^{-3})	2.853 and −1.435

$R_1 = \sum \| F_o| - |F_c \| / \sum |F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths (Å) for the title compound.

Ni(1)–O(3)	2.027(5)	Ni(1)–N(2)	2.040(7)
Ni(1)–N(1)	2.066(6)	Ni(1)–O(1W)	2.064(7)
Ni(1)–O(2W)	2.068(7)	Ni(1)–O(3W)	2.096(6)
Ni(2)–O(6W)	2.056(13)	Ni(2)–O(8W)	2.046(13)
Ni(2)–O(7W)	2.050(12)	Ni(2)–O(4)	2.106(6)
Ni(2)–O(5W)	2.127(12)	Ni(2)–O(4W)	2.107(12)
W(1)–O(1)	1.718(6)	W(1)–O(16)	1.889(5)
W(1)–O(15)	1.907(5)	W(1)–O(10)	1.943(5)
W(1)–O(8)#1	1.972(5)	W(1)–O(20)#1	2.255(5)
W(2)–O(2)	1.718(6)	W(2)–O(15)	1.901(5)
W(2)–O(14)	1.916(5)	W(2)–O(9)	1.931(5)
W(2)–O(11)	1.951(5)	W(2)–O(19)	2.202(5)
W(3)–O(3)	1.732(5)	W(3)–O(17)	1.895(5)
W(3)–O(13)	1.911(5)	W(3)–O(11)	1.929(5)
W(3)–O(12)	1.963(5)	W(3)–O(19)	2.117(5)
W(4)–O(4)	1.724(6)	W(4)–O(13)	1.910(5)
W(4)–O(18)	1.933(5)	W(4)–O(12)#1	1.931(5)
W(4)–O(9)#1	1.950(5)	W(4)–O(19)#1	2.185(5)
W(5)–O(5)	1.720(5)	W(5)–O(18)	1.880(5)
W(5)–O(17)	1.922(5)	W(5)–O(8)	1.922(5)
W(5)–O(7)	1.955(5)	W(5)–O(20)	2.221(5)
W(6)–O(6)	1.725(5)	W(6)–O(14)	1.910(5)
W(6)–O(7)	1.922(5)	W(6)–O(10)#1	1.927(5)
W(6)–O(16)	1.934(5)	W(6)–O(20)	2.224(4)

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

Table 3. Selected hydrogen bonds for the title compound.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1W)–H(1WB)···O(2)#2	0.96	2.35	2.880(9)	114.2
O(2W)–H(2WB)···O(13W)#2	0.96	2.60	3.302(16)	130.2
O(3W)–H(3WA)···O(8)#3	0.96	2.11	2.775(8)	125.3
O(3W)–H(3WB)···O(11W)	0.96	1.99	2.603(15)	119.7
O(4W)–H(4WA)···O(9W)	0.96	2.03	2.631(13)	118.7
O(4W)–H(4WB)···O(14W)#4	0.96	2.18	2.671(17)	110.7
O(5W)–H(5WA)···O(2W)#5	0.96	2.05	2.877(14)	143.6
O(5W)–H(5WB)···O(14W)	0.96	1.85	2.72(2)	149.9
O(5W)–H(5WB)···O(14W)#4	0.96	2.22	2.70(2)	110.1
O(6W)–H(6WA)···O(5)#3	0.96	2.36	3.094(17)	132.6
O(6W)–H(6WB)···O(12W)	0.96	2.37	2.90(2)	113.8
O(6W)–H(6WB)···O(2)#5	0.96	2.38	3.277(16)	155.2
O(7W)–H(7WB)···O(7)#3	0.96	2.17	2.797(12)	122.0
O(7W)–H(7WB)···O(2W)#5	0.96	2.53	3.121(14)	119.6
O(8W)–H(8WA)···O(9W)	0.96	2.23	3.125(16)	154.9
O(9W)–H(9WA)···O(4W)	0.96	2.12	2.631(13)	111.5
O(9W)–H(9WA)···O(8W)	0.96	2.65	3.125(16)	111.0
O(9W)–H(9WB)···O(13)	0.96	2.33	3.203(10)	150.6
O(9W)–H(9WB)···O(12)#1	0.96	2.42	3.116(9)	128.8
O(10W)–H(10B)···O(10)#6	0.96	2.26	3.216(10)	173.9
O(10W)–H(10C)···O(12W)	0.96	2.23	2.825(15)	119.0
O(11W)–H(11B)···O(7W)	0.96	2.23	2.949(19)	131.0
O(11W)–H(11B)···O(10)#7	0.96	2.57	3.037(14)	110.1
O(11W)–H(11C)···O(5)	0.96	2.21	2.910(15)	128.5
O(12W)–H(12C)···O(6W)	0.96	2.13	2.90(2)	136.2
O(12W)–H(12C)···O(2)#5	0.96	2.58	3.191(15)	122.2
O(13W)–H(13B)···O(7)	0.96	2.29	3.170(14)	152.5
O(13W)–H(13B)···O(17)	0.96	2.52	3.092(13)	118.6
O(13W)–H(13A)···O(2W)#2	0.96	2.43	3.302(16)	151.6
O(14W)–H(14A)···O(5W)	0.96	2.22	2.72(2)	111.6
O(14W)–H(14B)···O(4)#4	0.96	2.44	3.394(17)	175.8

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

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.

3. Results and discussion

3.1. *IR spectrum*

The IR spectrum of the title compound reveals four characteristic asymmetric vibration bands centered at 932, 886, 831 and 763 cm^{-1}, from the Keggin-type heteropolyoxoanions, namely, $\nu_{as}(W{=}O_t)$, $\nu_{as}(W{-}O_b)$, $\nu_{as}(W{-}O_d)$ and $\nu_{as}(W{-}O_c)$. Comparing the IR spectrum of the title compound with that of $[Bu_4N]_5H[H_2W_{12}O_{40}]$ [10], the W–O_b

band appears at a nearly identical frequency; the W=O_t and W–O_c vibrations have red-shifts of 12 and 21 cm^{-1}, respectively, resulting from the oxygen atom coordinated to the Ni(II) cations. Vibration bands centered at 1651, 1634, 1429, 1403 and 1362 cm^{-1} indicate the presence of 1, 10-phen. Comparing the IR spectrum of the title compound with free 1, 10-phen, the C–N band vibration frequency has a red-shift of 60 cm^{-1} from 1422 to 1362 cm^{-1}, which confirms 1, 10-phen coordinates to Ni(II) through nitrogen. The IR spectrum indicates that there is strong interaction between the polyoxoanions and metal-organic coordination cations in the solid state.

3.2. *UV spectrum*

The UV spectrum of the title compound in aqueous solution in the 400–190 nm region shows absorption bands at 215 nm and 255 nm, which are assigned to the pπ–dπ charge transfer absorptions $O_t \rightarrow W$ and $O_{d(c)} \rightarrow W$, respectively [11]. The latter is the characteristic absorption peak of the polyoxoanion, which is not affected by anion protonation. The UV spectrum of the title compound is very similar to those of the Keggin-type heteropolyanions $[XW_{12}O_{40}]^{n-}$ [12]. The above-mentioned result shows that the polyoxoanion $[H_2W_{12}O_{40}]^{6-}$ is a Keggin-type fragment with two protons in place of the heteroatom X.

3.3. *Electrochemical behavior*

The electrochemical behavior of the title compound was investigated in aqueous solution by means of cyclic voltammetry (CV). The metatungstate anion exhibits a kinetically stable and reproducible voltammetric pattern at least in the pH 5.85 and pH 4.45 media studied here. Figure 4 shows the cyclic voltammetric behaviors for 0.2 mol L^{-1} title compound in 0.5 mol L^{-1} NaCl pH = 5.85 and pH = 4.45 aqueous solution at scan rate 20 m V s^{-1}. In the pH 5.85 medium, in the potential range from −0.9 V to 1.1 V, one reversible redox peak is observed with midpoint potential (E_{mid}) of −0.465 V ($E_{pc} = -0.738$ V and $E_{pa} = -0.191$ V), which is involved in one-electron charge-transfer processes, where $E_{mid} = (E_{pc} + E_{pa})/2$; E_{pc} and E_{pa} are cathodic and anodic peak potentials. In the pH 4.45 medium, one one-electron charge-transfer reversible redox peak is still observed with midpoint potential (E_{mid}) of −0.405 V ($E_{pc} = -0.660$ V and $E_{pa} = -0.150$ V). From the above analysis, it is obvious that, when the pH value of medium varies from 5.85 to 4.45, the peak potential shifts by 60 mV toward the positive direction, indicating that as the pH value of the solution was lowered, the oxidation capacity of the polyoxoanion became stronger. This may arise from protonation of the polyoxoanion.

3.4. *Descriptions of the structures*

Molecular structure representation of the title compound with the labeling scheme is shown in figure 1. The ball-and-stick and polyhedral arrangement of the title compound polyoxoanion is given in figure 2. The title compound consists of two supporting $[Ni(phen)(H_2O)_3]^{2+}$ coordination cations, one supporting $[Ni(H_2O)_5]^{2+}$ ion, six H_2O

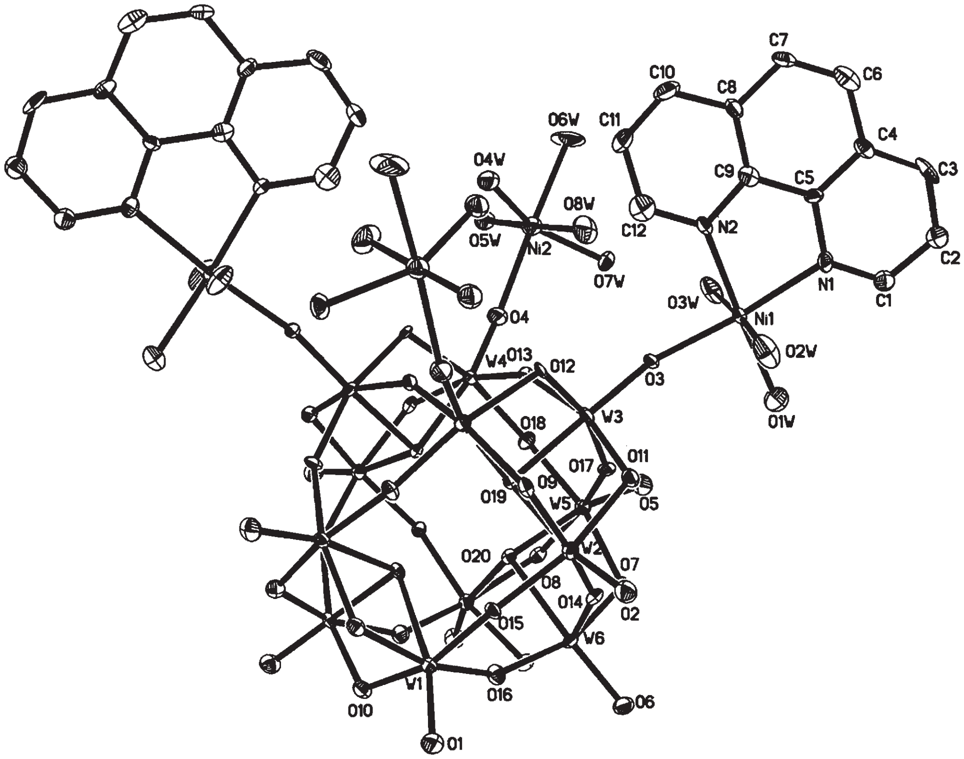

Figure 1. A fragment of the title compound with the atomic labeling scheme.

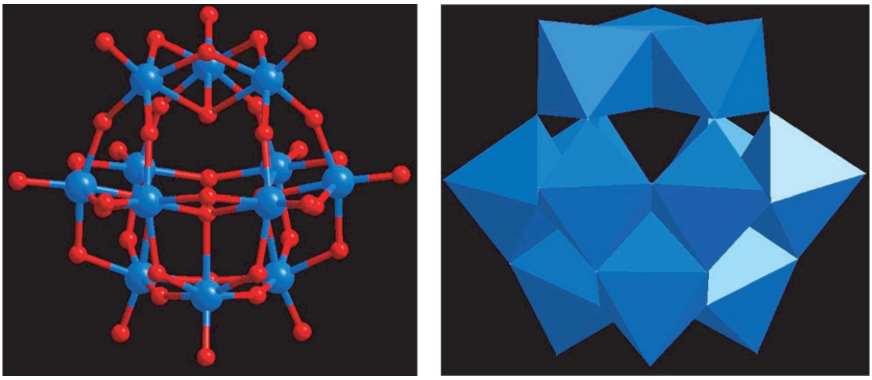

Figure 2. The ball-and-stick (left) and polyhedral (right) representation of the title polyoxoanion.

molecules of crystallization and one metatungstate $[H_2W_{12}O_{40}]^{6-}$ polyoxoanion approaching an effective T_d point symmetry. The two supporting $[Ni(phen)(H_2O)_3]^{2+}$ coordination cations are twin-distributed by coordinating to the terminal oxygen atoms from the $[H_2W_{12}O_{40}]^{6-}$ polyoxoanion through the Ni–O–W links. In addition, the site occupancy of $[Ni(H_2O)_5]^{2+}$ ion is 0.5. The two supporting "one-half" $[Ni(H_2O)_5]^{2+}$ ions are also symmetrically situated in the opposite direction combined with the $[H_2W_{12}O_{40}]^{6-}$ polyoxoanion through the Ni–O–W links. Therefore, by this architectural motif, organic-inorganic hybrid four nickel cations supporting metatungstate is formed. The structure of the dodecatungstate ion $[H_2W_{12}O_{40}]^{6-}$ in the title compound is very similar to $[Cu(2,2'\text{-bipy})_3]_2H_2[H_2W_{12}O_{40}] \cdot 4.5H_2O$ [13], $Rb_4H_4[H_2W_{12}O_{40}] \cdot 6H_2O$ [14], $[N(CH_3)_2]_6[H_2W_{12}O_{40}] \cdot 4H_2O$ and $[N(CH_3)_4]_6[H_2W_{12}O_{40}] \cdot 2H_2O$ [15]. Generally, the Keggin cluster $[XW_{12}O_{40}]^{n-}$, reported by Keggin in 1934 [16], holds a heteroatom X such as Si in $TMA_4[SiW_{12}O_{40}]$ [17], P in $(H_5O_2^+)_3[PW_{12}O_{40}]^{3-}$ [18]. The structure with three hydrogen atoms per cluster $[H_3W_{12}O_{40}]^{5-}$ was also reported [19], but this composition was based on charge balance and not on complete structure determination.

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(19), O(20), O(19A) and O(20A)] form an almost close-packed structure with a tetrahedral cavity inside the cluster, which is occupied by two disordered H atoms based on earlier NMR study [20] and neutron diffraction [21]. The polyoxoanion $[H_2W_{12}O_{40}]^{6-}$ exhibits the usual arrangement of four W_3O_{13} groups, each in association with three edge-sharing WO_6 octahedra. This structure is in good agreement with that previously reported [15]. The oxygen atoms can be divided into four categories according to their different coordination environment in the polyoxoanions: O_t (terminal oxygen atoms connecting one W atom), O_b (atoms located in the shared corners between two W_3O_{13} units), O_c (oxygen atoms connecting edge-sharing WO_6 octahedra in the same W_3O_{13} units) and O_d (oxygen atoms connecting the three W atoms). Relevant W–O bonds can be classified into four groups: W–O_t 1.718 (6)–1.732(5) Å, W–O_b 1.880(5)–1.963(5) Å, W–O_c 1.889(5)–1.972(5) Å, W–O_d 2.117(5)–2.255(5) Å, and their average distances are 1.723 Å, 1.919 Å, 1.931 Å and 2.201 Å, respectively. The W3–O3 and W4–O4 distances of 1.732(5) Å and 1.724(6) Å are longer than the average W–O_t distance of 1.720 Å attributable to O3 and O4 atoms coordinating to Ni(1) and Ni(2) atoms. These bond lengths are almost consistent with the previous literature [18]. The four kinds of W–O distances are in good agreement with the υ_{as}(W–O_t), υ_{as}(W–O_b), υ_{as}(W–Oc_b) and υ_{as}(W–O_d) vibration modes of the IR spectrum.

The nickel atoms can be divided into two categories according to their coordination environment. The coordination geometries of all the Ni^{II} ions are distorted octahedral; Ni(1) is coordinated by three water molecules, two nitrogen atoms from phen and one terminal oxygen atom from the polyoxoanion $[H_2W_{12}O_{40}]^{6-}$. The Ni–O_t distance is 2.027(5) Å, the Ni–O_W distances are in the range of 2.064(7)–2.096(6) Å, the Ni–N distances are from 2.040(7) Å to 2.066(6) Å, Ni(2) ion is coordinated by five water molecules and one oxygen atom from the framework of the polyoxoanion $[H_2W_{12}O_{40}]^{6-}$ with the Ni–O_t distance of 2.106(6) Å and the Ni–O_W distances of 2.046(13)–2.127(12) Å.

The presence of numerous heavy atoms in the structure precludes determination of hydrogen atom positions. Although we cannot precisely locate the sites of the two H^+ ions in $[H_2W_{12}O_{40}]^{6-}$ by X-ray diffraction, bond valence sum calculations (BVS) [22] locate the H^+ ions. The BVS values of the O19 and O20 atoms by means of equation (1)

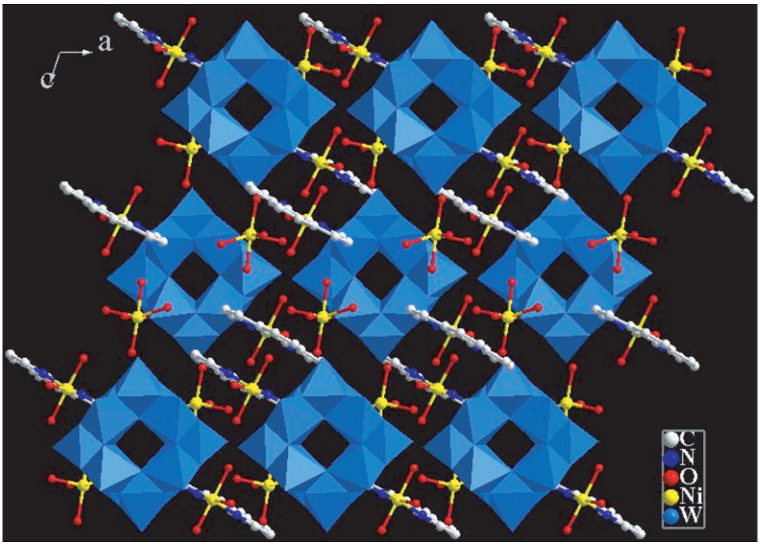

Figure 3. Stacking new of the title compound along the crystallographic *b* axis. All hydrogen atoms, water molecules of crystallization and hydrogen bonding interactions are omitted for clarity.

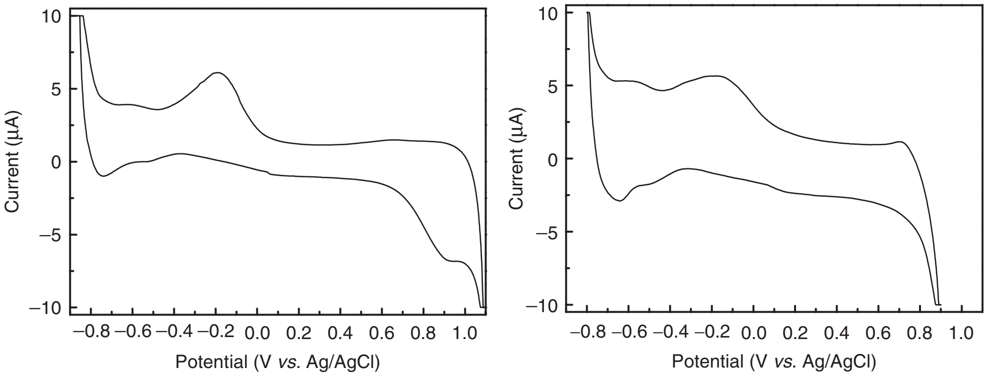

Figure 4. Cyclic voltammograms of a 0.2 mm solution of the title compound at pH 5.85 (left) pH 4.45 (right) in aqueous solution containing 0.5 m NaCl + HCl at scan rate 20 mVs^{-1}.

are 1.528 and 1.279, respectively, far from 2, strongly suggesting that O19 and O20 are protonated.

$$V_i = \sum_j S_{ij} = \sum_j \exp\left(\frac{r'_{\mathrm{o}} - r_{ij}}{B}\right). \qquad (1)$$

The presence of coordination water and lattice water molecules allows formation of the three-dimensional supramolecular architecture in the title compound (figure 3). The supramolecular architecture is based on hydrogen bonding interactions between the surface oxygen donors from the $[H_2W_{12}O_{40}]^{6-}$ polyoxoanions and the water molecule acceptors with Ow–H$\cdots$Os distances of 2.775(8)–3.394(17) Å and the Ow–H$\cdots$Os bond angles of 114.2–175.8° (Ow and Os represent the water molecules and the surface oxygen atoms from $[H_2W_{12}O_{40}]^{6-}$). Furthermore, the weak $\pi\cdots\pi$

stacking interactions between adjacent phenanthroline ligands assist in formation of the supramolecular network.

4. Conclusions

An organic-inorganic hybrid polyoxometalate containing dodecatungstate building blocks has been synthesized, structurally characterized and investigated by electrochemistry. The title compound represents the first nickel-phenanthroline coordination cation supporting a metatungstate derivative. The synthesis of the title compound offers a complementary method for preparing other novel organic-inorganic hybrid metatungstate derivatives.

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