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Three inorganic–organic hybrid compounds based on Keggin polyoxometalate and transition metal complexes: crystal structures and electrochemical properties

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Polyoxometalate (POM)-based coordination polymers, $[Cu(L)_2][SiW_{12}O_{40}]\cdot 4py\cdot H_2O$ (**1**), $[Ag(py)_2]_4[SiW_{12}O_{40}]$ (**2**) and $[Co(L)_3]_2[SiW_{12}O_{40}]\cdot py\cdot 7H_2O$ (**3**) (L = pyridine-2-carboxylic acid, py = pyridine), have been obtained hydrothermally and characterized by elemental analyses, IR and single-crystal X-ray diffraction analyses. Electrochemical properties are also investigated.

Keywords: Inorganic–organic hybrids; Polyoxometalates; Electrochemical properties

1. Introduction

Polyoxometalate (POM)-supported inorganic–organic hybrid materials have attracted attention for intriguing architectures and properties with potential applications in catalysis, gas storage, selective absorption, magnetism, and medicine [1–10]. A series of inorganic–organic hybrid materials based on POMs and transition metal complexes have been assembled [11–14]. However, design and synthesis of POM-based inorganic–organic hybrid materials remain an arduous task.

Herein, three POM-based coordination polymers, $[Cu(L)_2][SiW_{12}O_{40}]\cdot 4py\cdot H_2O$ (**1**), $[Ag(py)_2]_4[SiW_{12}O_{40}]$ (**2**) and $[Co(L)_3]_2[SiW_{12}O_{40}]\cdot py\cdot 7H_2O$ (**3**) (L = pyridine-2-carboxylic acid, py = pyridine), have been synthesized hydrothermally and characterized.

2. Experiment

2.1. *Materials and methods*

All reagents were purchased commercially and used without purification. Infrared spectra were obtained (as KBr pressed pellets) with a Nicolet 170SXFT/IR spectrometer. C, H, and N elemental analyses were performed with a Perkin–Elmer 2400 CHN elemental

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analyzer. All electrochemical measurements were carried out with a CHI 660 electrochemical workstation at room temperature. Cyclic voltammograms were recorded with a 384B polarographic analyzer. A modified carbon-paste electrode (CPE) was fabricated as follows: graphite powder (0.5 g) and compound (25 mg) were mixed and ground together in an agate mortar with a pestle to achieve an even, dry mixture. Paraffin (0.3 mL) was then added to the mixture, which was stirred with a glass rod. The homogenized mixture was used to pack 3 mm inner-diameter glass tubes, and the surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode. A typical three-electrode cell with a CPE working electrode, a platinum counter electrode, and a silver/silver chloride reference electrode was used for the voltammetry and impedance experiments. The Ac Impedance Spectroscopy was carried out in 0.4 M H_2SO_4, 0.4 M KNO_3, and 5.0×10^{-3} M $K_3[Fe(CN)_6]$ aqueous solution.

2.2. *Preparation of the compounds*

2.2.1. Synthesis of $[Cu(L)_2][SiW_{12}O_{40}]\cdot 4py\cdot H_2O$ (1). A mixture of $H_4SiW_{12}O_{40}\cdot 12H_2O$ (0.282 g, 0.1 mmol), $Cu(NO_3)_2\cdot 6H_2O$ (0.06 g, 0.25 mmol), and pyridine-2,6-dicarboxylate (0.085 g, 0.5 mmol) was dissolved in 10 mL distilled water. The mixture was sealed into a 25 mL Teflon-lined autoclave and kept under autogenous pressure at 160 °C for 3 d. After slow cooling to room temperature, blue block crystals of **1** were filtered and washed with distilled water. (Yield 41% based on W). Elemental Anal. Calcd for **1** (wt. %): C, 10.91; H, 0.85; N, 2.39. Found: C, 11.01; H, 0.91; N, 2.43.

2.2.2. Synthesis of $[Ag(py)_2]_4[SiW_{12}O_{40}]$ (2). The preparation was similar to that for **1**, except that $Cu(NO_3)_2\cdot 6H_2O$ was replaced by $AgNO_3$. Yellow block crystals were filtered, washed with distilled water, and dried in a desiccator at room temperature to give a yield of 38% based on W. Elemental Anal. Calcd for **2** (wt.%): C, 12.18; H, 1.01; N, 2.84. Found: C, 12.25; H, 1.11; N, 2.93.

2.2.3. Synthesis of $[Co(L)_3]_2[SiW_{12}O_{40}]\cdot py\cdot 7H_2O$ (3). The preparation was similar to that for **1**, except that $Cu(NO_3)_3\cdot 6H_2O$ was replaced by $Co(NO_3)_3\cdot 6H_2O$. Red block crystals were filtered, washed with distilled water, and dried in a desiccator at room temperature to give 32% based on W. Elemental Anal. Calcd for **3** (wt.%): C, 12.51; H, 1.09; N, 2.49. Found: C, 12.61; H, 1.11; N, 2.53.

2.3. *X-ray crystallography*

Intensity data of **1–3** were collected with a Bruker Smart Apex CCD area-detector diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at room temperature. Absorption corrections were applied using the multiscan program SADABS. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL-97 on a legend computer [15]. All nonhydrogen atoms were refined anisotropically. Hydrogens were located in calculated positions and refined by using

Table 1. Crystal data and structure refinements for 1–3.

	1	**2**	**3**
Formula	$C_{32}H_{30}CuN_6O_{45}SiW_{12}$	$C_{40}H_{40}Ag_4N_8O_{40}SiW_{12}$	$C_{41}H_{43}Co_2N_7O_{59}SiW_{12}$
Weight	3516.45	3938.57	3929.97
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*P 1 21/n 1*	*P−1*	*P−1*
a/Å	12.999(2)	12.0676(15)	12.4157(15)
b/Å	14.519(2)	13.3724(15)	13.6242(14)
c/Å	16.661(3)	13.4487(15)	14.4001(17)
α/°	90	107.0230(10)	62.273(5)
β/°	99.539(2)	103.3560(10)	80.4700(10)
γ/°	90	114.8300(10)	77.743(2)
T/K	150(2)	150(2)	150(2)
V/Å^3	3101.1(9)	1719.6(3)	2100.7(4)
D_{calc}/g cm^{-3}	3.7658	3.80313	3.10634
F(000)	3110	1746	1766
Z	2	1	1
Absorption coefficient	22.615	21.197	16.855
Goodness-of-fit on F^2	1.104	1.080	1.100
Data/restraints/parameters	5432/150/422	5978/108/494	7296/102/599
R_{int}	0.0504	0.0428	0.0332
R_1 [$I > 2\sigma(I)$][a]	0.0579	0.0685	0.0635
wR_2 (all data)[b]	0.1666	0.1886	0.1715

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

a riding model. The crystal and structure refinement data for **1–3** are summarized in table 1. Selected bond lengths (Å) and angles (°) for **1–3** are listed in tables S1, S2, and S3.

3. Results and discussion

3.1. *Synthesis*

Compounds **1, 2,** and **3** were synthesized in a similar way, but exhibit different structures. Pyridine-2,6-dicarboxylate decomposes in the presence of metal ion for **1–3**. Especially for **2**, pyridine-2,6-dicarboxylate decomposes completely to pyridine in the presence of Ag^+.

3.2. *Structure description*

The structure of the Keggin core is unexceptional in **1–3**, including a central {SiO4} tetrahedron surrounded by 12 {WO6} octahedra arranged in four groups of three edge-sharing octahedral units {W3O13}.

As shown in figure 1, single-crystal X-ray structural analysis reveals that the structure of **1** consists of one Cu^{II}, two L, four pyridines, one $[SiW_{12}O_{40}]^{4-}$, and one water molecule. Cu1 is six-coordinate by two nitrogen atoms and two oxygen atoms from two L, and two oxygen atoms from different $[SiW_{12}O_{40}]^{4-}$ anions (Cu1–O19 = 2.720(4) Å). Therefore, $[SiW_{12}O_{40}]^{4-}$ as a bidentate ligand utilizes two terminal oxygen atoms to link

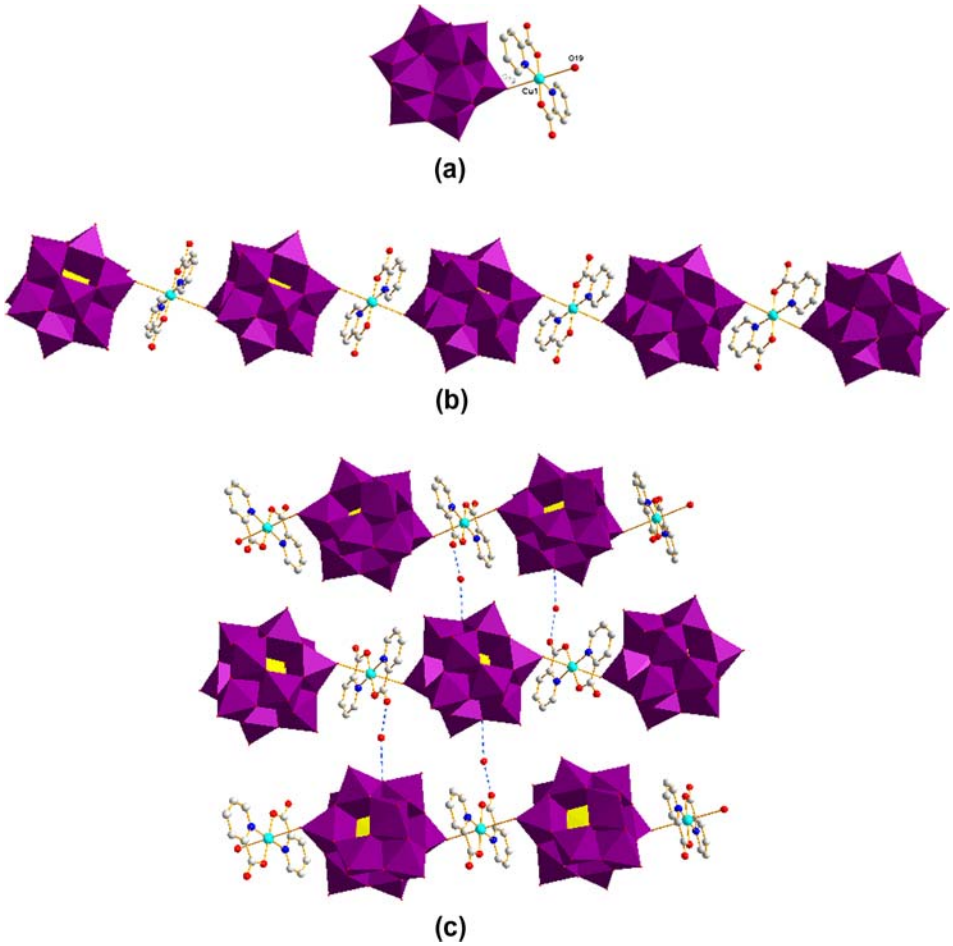

Figure 1. (a) The asymmetric unit of **1**. Color code: C (gray balls), N (blue balls), O (red balls), Cu (turquoise balls), W (purple octahedra), and Si (yellow tetrahedra). (b) The 1D chain structure of **1**. (c) The 2D network structure of **1**.

Cu ions to generate a 1D chain. 2D supramolecular assembly is finally formed by hydrogen-bonding interactions (table S4).

Single-crystal X-ray structural analysis reveals that the structure of **2** contains four Ag^I ions, eight L, and one $[SiW_{12}O_{40}]^{4-}$. Ag1 is three-coordinate by two py and one oxygen from $[SiW_{12}O_{40}]^{4-}$ (see figure 2). Thus, two adjacent $[SiW_{12}O_{40}]^{4-}$ anions are connected through noncovalent Ag–O interactions to form a 1D chain. The Ag1–O17 distance is 2.984 Å, shorter than the sum of the van der Waals radii of Ag and O (3.20 Å) [16]. Finally, a 2D supramolecular network is formed by Ag–O interactions.

Single-crystal X-ray structural analysis reveals that the structure of **3** contains two Co^{II} ions, six L, one pyridine, one $[SiW_{12}O_{40}]^{4-}$, and seven waters. Co1 is six-coordinate with two nitrogen atoms and two oxygen atoms from three L (as shown in figure 3). The 3D supramolecular assembly is formed by hydrogen-bonding interactions (table S5).

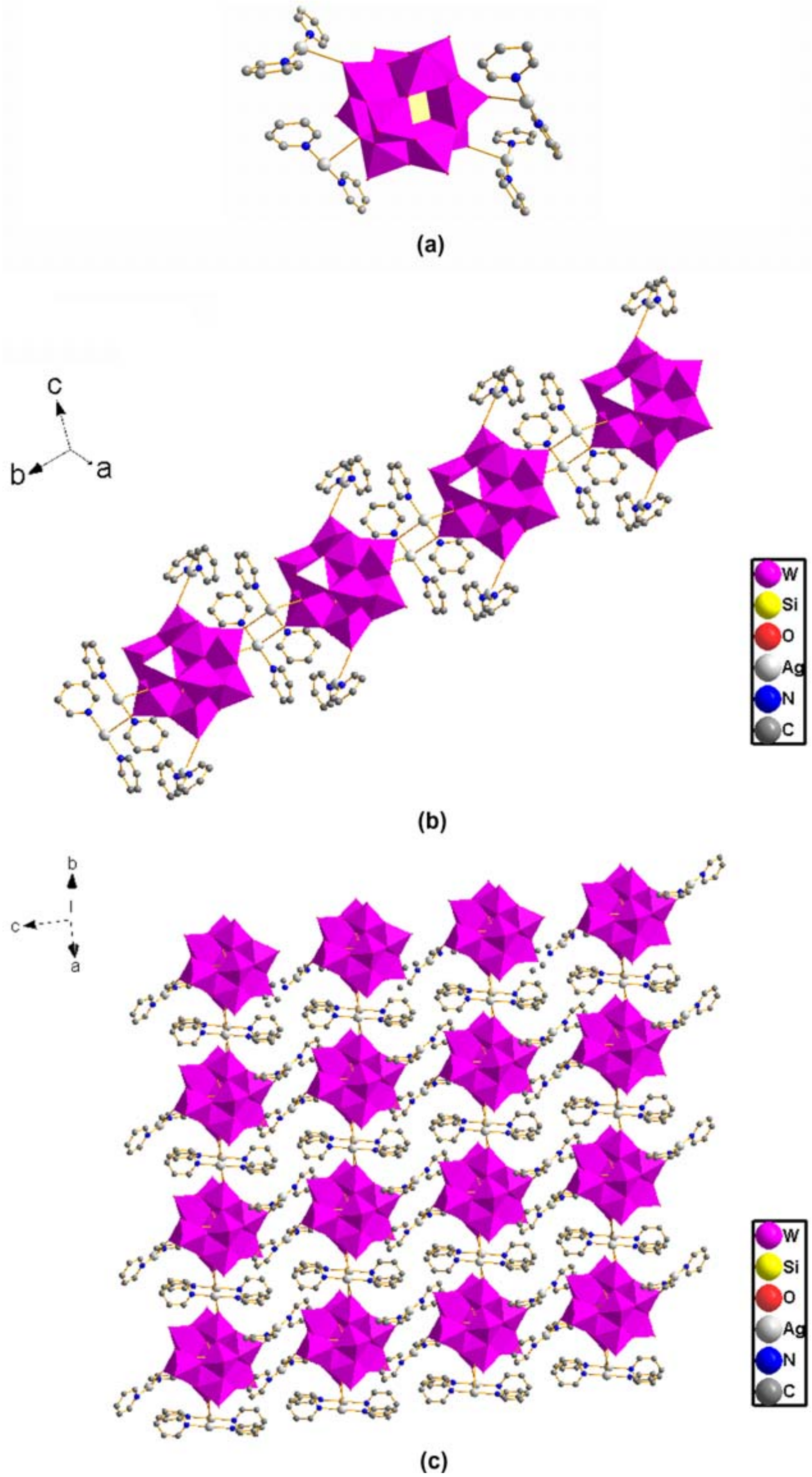

Figure 2. (a) The asymmetric unit of **2**. (b) The 1D chain structure of **2**. (c) The 2D network structure of **2**.

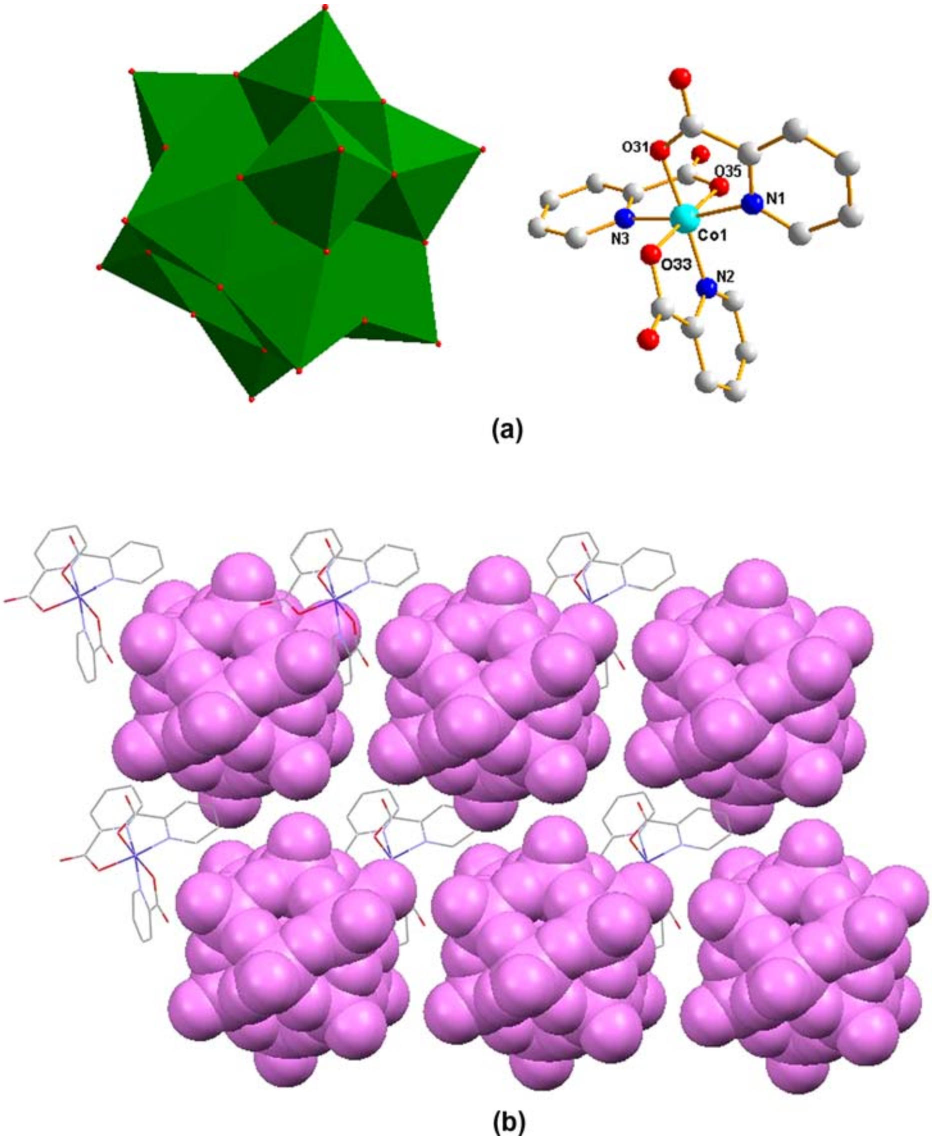

Figure 3. (a) The asymmetric unit of **3**. Color code: C (gray balls), N (blue balls), O (red balls), Co (turquoise balls), W (green octahedra), and Si (yellow tetrahedra). (b) The 3D structure of **3**.

3.3. *IR spectra*

IR spectra of **1, 2,** and **3** are shown in figures S1, S2, and S3. Characteristic peaks at 1055, 971, 914, 802, and 758 cm^{-1} are attributed to the Keggin polyoxoanion, and peaks at 1610–1100 cm^{-1} are attributed to ligand.

3.4. *Cyclic voltammetry*

Cyclic voltammetric behavior of **1**-CPE in 1 M H_2SO_4 was recorded (see figure 4), exhibiting three reversible redox peaks II–II′, III–III′, and IV–IV′ with half-wave potentials $E_{½} = (E_{pa} + E_{pc})/2 = 0.201$ (II–II′), –0.258 (III–III′), –0.602 (IV–IV′) V (scan rate: 0.025 Vs^{-1}) in the potential range +0.3 to −0.8 V, attributable to $[SiW_{12}O_{40}]^{4-}$. One irreversible anodic peak I exists with potential of +0.750 V assigned to oxidation of copper. **1**-CPE showed remarkable stability ascribed to the insolubility of the inorganic–organic hybrid material.

3.5. *Ac Impedance Spectroscopy*

Ac Impedance Spectroscopy of **1**-CPE, **2**-CPE, and **3**-CPE in H_2SO_4, KNO_3, and $K_3[Fe(CN)_6]$ aqueous solutions was studied. Ac Impedance Spectroscopy provides information about the capacity of electron transfer or activation for electrode. Larger impedance values indicate less capacity of electron transfer or reacting activation for the electrode. **1**-CPE shows similar semicircle in three different aqueous solutions except the diameter of the semicircle (see figure S4). The impedance values in $K_3[Fe(CN)_6]$ aqueous solution is higher than KNO_3 and H_2SO_4 aqueous solutions. For **1**-CPE, the capacity of electron transfer and reacting activation is H_2SO_4 solution > KNO_3 solution > $K_3[Fe(CN)_6]$ solution. For **2**-CPE, the Ac Impedance spectra in H_2SO_4 aqueous solution shows an inclined line and the other similar semicircles (see figure S5). For **2**-CPE, the capacity of electron transfer and reacting activation is KNO_3 solution > $K_3[Fe(CN)_6]$ solution > H_2SO_4 solution. **3**-CPE shows similar semicircles in different aqueous solutions [see figure 5(a)]. For **3**-CPE, the capacity of electron transfer and reacting activation is KNO_3 solution > H_2SO_4 solution > $K_3[Fe(CN)_6]$. Similarly, the Ac Impedance spectra of three electrodes in the same aqueous solution were also compared. In H_2SO_4 aqueous solution, **1**-CPE, **2**-CPE, and **3**-CPE show semicircles [see figure 5(b)] with capacity of electron transfer and

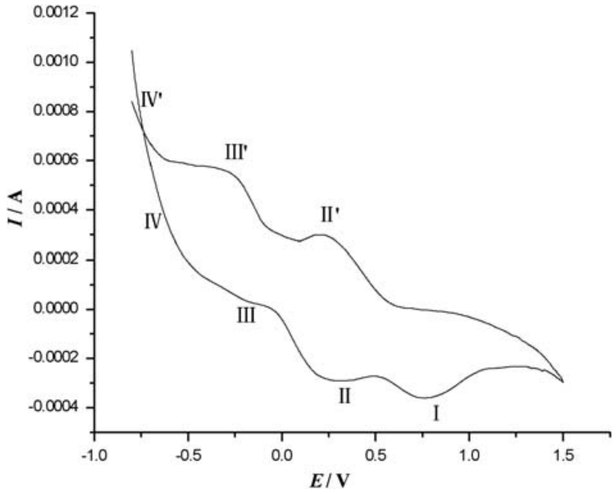

Figure 4. Cyclic voltammograms of **1**–CPE (CPE = carbon-paste electrode) in 1 M H_2SO_4 solution at scan rates 0.025 $V s^{-1}$.

reacting activation **1**-CPE > **3**-CPE > **2**-CPE. In $K_3[Fe(CN)_6]$ solution, the electrodes show similar semicircles except diameter of the semicircle with descending order **1**-CPE, **3**-CPE, and **2**-CPE (see figure S6). In $K_3[Fe(CN)_6]$ solution, the capacity of electron transfer and reacting activation is **2**-CPE > **3**-CPE > **1**-CPE. In KNO_3 aqueous solution, **3**-CPE shows an inclined line and **1**-CPE and **2**-CPE show semicircles (see figure S7). In KNO_3 solution, the capacity of electron transfer and reacting activation is **1**-CPE > **2**-CPE > **3**-CPE. The plot of semicircle shows a dynamics-controlled process and an inclined line is diffusion-controlled [17]. In addition, the Ac Impedance spectra depend on the nature of electrode, ionic or electron transport, time, temperature, etc.

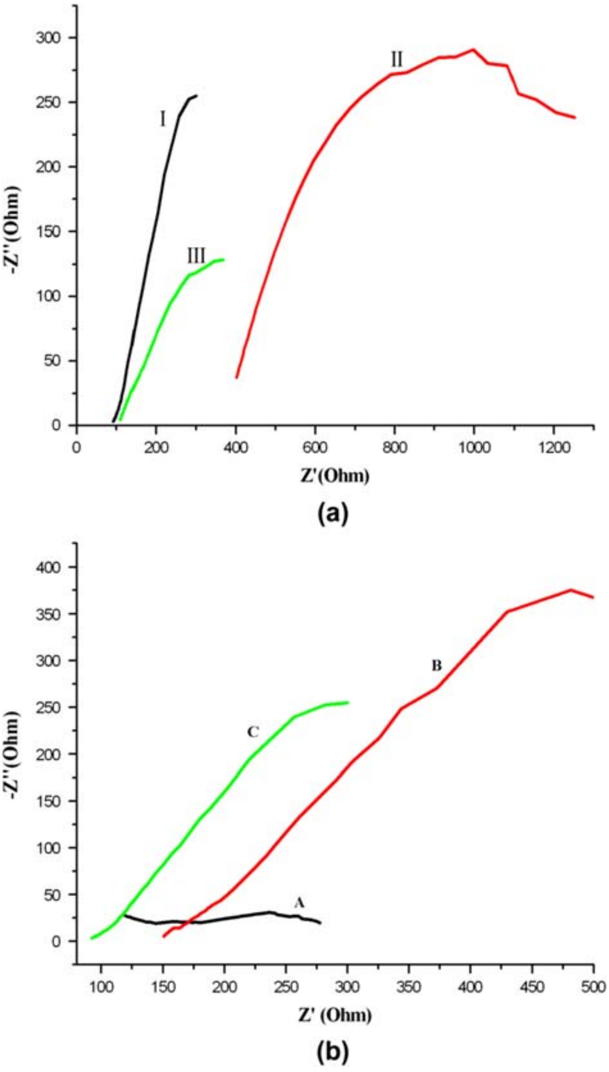

Figure 5. (a) Ac Impedance Spectra of **3**–CPE in (I) H_2SO_4, (II) $K_3[Fe(CN)_6]$, and (III) KNO_3 aqueous solution. (b) Ac Impedance Spectra of **1**–CPE (A), **2**–CPE (B), and **3**–CPE (C) in H_2SO_4 aqueous solution.

4. Conclusion

Three inorganic–organic compounds have been hydrothermally synthesized; metal ion plays important roles in decarboxylation and forming of the final product, similar to some complexes [18]. This work enriches the family of hybrid compounds based on Keggin-type $[SiW_{12}O_{40}]^{4-}$ and transition metal complexes by hydrothermal decarboxylation. Electrochemical properties show that the Ac Impedance Spectroscopy may provide meaningful and practical information for applications.

Supplementary material

Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 782452-782454 for **1**, **2,** and **3**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif. IR, Ac Impedance Spectra, tables of selected bond lengths (Å) and angles (°), and tables of selected hydrogen bond interactions are available in supporting information.

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