

RESEARCH ARTICLE



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tant new member of hexa-nuclear nickel cluster substituted TMSP, in which an unusual boat-like $\{\text{Ni}_6(\text{OH})(\text{BO}_3)_2(\text{dien})_2\}$ cluster was observed for the first time. In both compounds, interesting structural transformations based on the $\{\text{A-}\alpha\text{-SiW}_9\text{O}_{34}\}$ unit were observed. Additionally, the photocatalytic activity, magnetic behaviors, and the proton conduction performance of the compounds were initially evaluated.

2. Experimental section

2.1 Materials

All chemical reagents were purchased and directly used without purification. $\text{Na}_{10}[\text{A-}\alpha\text{-SiW}_9\text{O}_{34}]\cdot 18\text{H}_2\text{O}$ was synthesized according to the literature method.³⁷ IR spectra were recorded on an Opus Vertex 70 FT-IR infrared spectrophotometer in the range of 4000–500 cm^{-1} . Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on an Ultima2 spectrometer. Elemental analyses of C, H, and N were conducted on a Vario EL III elemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected on a Philips X'Pert-MPD diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Thermogravimetric analysis was conducted on a Mettler Toledo TGA/SDTA 851^e analyzer under an air-flow atmosphere with a 10 $^\circ\text{C min}^{-1}$ heating rate in the temperature of 30–800 $^\circ\text{C}$. UV-vis diffuse reflection spectra were collected

Table 1 Crystal data and structure refinements for compounds 1–2

Compound	1	2
Empirical formula	H ₁₅₉ C ₈ N ₄ Na ₁₉ Ni ₁₂ O ₁₉₉ P ₆ Si ₃ W ₃₁	H _{160.5} B ₄ C ₁₆ N ₁₂ O ₂₀₂ K _{2.5} NaNi ₁₂ W ₄₀
ρ_r (g mol ⁻¹)	10 047.14	11 650.91
Temperature/K	175(2)	175(2)
Crystal system	Monoclinic	Trigonal
Space group	2 ₁ /	3 ₂ 21
a (Å)	20.4528(8)	35.1946(18)
b (Å)	24.8351(9)	35.1946(18)
c (Å)	24.7637(9)	49.109(3)
α (°)	90.00	90
β (°)	113.0150(10)	90
γ (°)	90.00	120
V (Å ³)	11 577.4(8)	52 680(6)
Z	2	6
ρ_{calcd} (g cm ⁻³)	2.882	2.204
μ mm ⁻¹	16.460	13.772
(000)	8910	30 674
Crystal size/mm ³	0.2 × 0.15 × 0.2	0.2 × 0.12 × 0.2
Theta range/°	1.843 to 25.059	1.336 to 25.073
R_{int}	0.0260	0.0944
Goof	1.043	1.051
[> 2 σ]	$w_1 = 0.0246$	$w_1 = 0.0579$
(all data)	$w_2 = 0.0601$	$w_2 = 0.1275$
	$w_1 = 0.0277$	$w_1 = 0.0749$
	$w_2 = 0.0613$	$w_2 = 0.1352$

$$w_1 = \sum(|o| - |c|) / \sum |o|, w_2 = \left\{ \sum [w(\frac{2}{o} - \frac{2}{c})^2] / \sum [w(\frac{2}{o})^2] \right\}^{1/2}.$$

like {W₄O₁₀(OH)[PO₂(OH)₂]₂} ({P₂W₄}) (Fig. 1e) unit, which has never been found before. The {P₂W₄} unit can be viewed as a {W₄O₁₀(OH)} subunit consisting of four corner-sharing {WO₆} octahedra further decorated by two {PO₄} tetrahedra in the gaps at both ends. These additional {WO₆} octahedra should be generated from degradation of the starting {A-SiW₉} units under the basic condition. So far, isopolyoxotungstate fragments based on a number of {WO₆} octahedra which serve as a linker to construct novel multilacunary POM fragments are still rare. A representative example is a {Sb₂W₂₀O₇₃} fragment comprised of two {SbW₉O₃₄} units and an isopolytungstate fragment based on two {WO₆} octahedra.³⁸ Therefore, the {A-P₂Si₂W₂₂} subunit can be considered as an interesting multi-dentate oxo ligand to incorporate with the {Ni₁₂} cluster. The central {Ni₁₂} (Fig. 1f) cluster can be described as three tetrahedral {Ni₄(OH)₃} (Fig. 1g) building blocks connected by a μ_3 -{PO₄} tetrahedron and three μ_4 -{PO₄} tetrahedra. In other words, the whole polyanion of **1** can also be understood as a {Ni₃(PO₄)₄} core enveloped by three {(NiOH)₃(A- α -SiW₉O₃₄)} units, in which the {Ni₃(PO₄)₄} core displays a {Ni₃O₄} (Fig. 1h) quasi-cubane structure, and an extra {P₂W₄} cluster further anchors two trilacunary subunits. All the nickel ions in the {Ni₁₂} cluster display a distorted octahedral coordination geometry, and the Ni–O bond lengths are in the range of 1.947(19)–2.230(18) Å. Bond valence sum (BVS) calculations manifest that all the nickel ions are in the +2 oxidation state and partial O atoms are in the -1 valence state (Tables S2–S4, ESI[†]). It is noteworthy that such a {Ni₁₂} cluster is different from those reported nickel clusters containing twelve nickel ions in reported compounds including [Ni₁₂(OH)₉WO₄(W₇O₂₆(OH))(PW₉O₃₄)₃]^{25–},³⁹ [Ni₁₂(OH)₉(CO₃)₃(PO₄)(SiW₉O₃₄)₃]^{24–},²⁵ and [(BO₃)₃PO₄Ni₁₂O₉(SiW₉O₃₄)₃]^{36–}.⁴⁰ The {Ni₁₂} cluster in **1** was stabilized by four {PO₄} tetrahedra besides the

POM units, while the nickel clusters in reported examples were decorated by {WO₄} tetrahedra or {CO₃/BO₃} triangles mixed {PO₄} with tetrahedra.

3.2 Crystal structure of H_{26.5}K_{2.5}Na(H₂O)₁₆[Ni₆(OH)(BO₃)₂(dien)₂(B- α -S W₁₀O₃₇)₂]₂·24H₂O (**2**)

Single crystal X-ray diffraction analysis reveals that **2** crystallizes in the trigonal 3₂21 chiral space group. The asymmetric unit of **2** contains two identical Ni₆-substituted polyanions (Fig. 2a and b), each of which is composed of two dilacunary B- α -{SiW₁₀O₃₇} ({B-SiW₁₀}) units and a hexa-nuclear nickel cluster {Ni₆(OH)(BO₃)₂(dien)₂} ({Ni₆}, Fig. 2c). The {B-SiW₁₀} (Fig. 2d) comes from structural transformation from the starting {A-SiW₉} units. The central Ni₆ cluster can be regarded as a boat-like structure consisting of six nickel ions and is further stabilized by two dien ligands (Fig. 2e) and two {BO₃} units (Fig. 2f). The four Ni atoms situated at the bottom of the boat are coordinated by five O atoms and one OH group. The other two Ni atoms at the bow and stern of the boat are coordinated by three N atoms from a dien ligand and three O atoms, respectively (Fig. 2g). All the nickel atoms in this {Ni₆} cluster adopt a distorted octahedral coordination geometry with the Ni–O bond lengths in the range of 1.956(19)–2.332(18) Å and the Ni–N bond lengths in the ranges of 2.022–2.100 Å. The BO₃ units is from the depolymerization of the starting Li₂B₄O₇ and K₂B₁₀O₁₆·8H₂O, and the B–O bond lengths of the {BO₃} segment are in the range of 1.313–1.438 Å. Up to now, the boron species have been seldom found in POM chemistry,³⁹ and such a {Ni₆} cluster decorated by two {BO₃} units has not been found before. BVS calculations manifested that all the nickel ions are in the +2 oxidation state and partial O

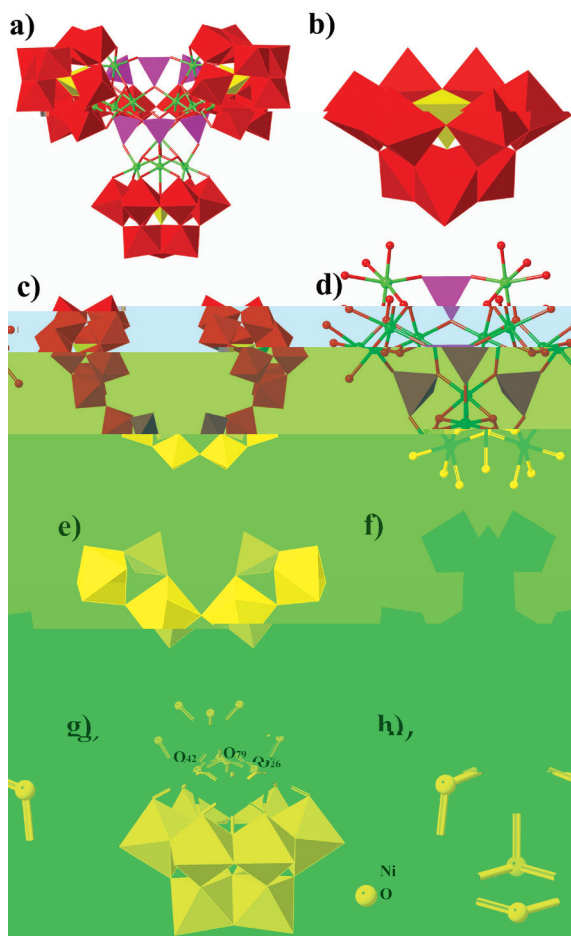


Fig. 1 (a) Combined polyhedral/ball-and-stick representation of the polyanion in **1**. (b) The trilacunary Keggin polyanion {A-SiW₉}. (c) The {A-P₂Si₂W₂₂} fragment. (d) The connection diagram of the {Ni₁₂} core and four {PO₄}. (e) The belt-like {P₂W₄} unit. (f) The {Ni₁₂} core. (g) The {Ni₄(OH)₃(A-α-SiW₉O₃₄)} unit. (h) View of the {Ni₃O₄} quasi-cubane structure. Color legend: WO₆, red octahedra; Ni^{II}, green balls; NiO₆, green octahedra; SiO₄, yellow tetrahedron; PO₄, purple tetrahedron.

atoms are in the -1 valence state (Table S5, ESI†). Although Gd(NO₃)₃ does not crystallize in the structure, it may show subtle influence in adjusting the ionic strength or the pH value of the reaction system, which is crucial for the formation of compound **2**. Interestingly, the boat-like {Ni₆} cluster in **2** is different from other previously reported hexa-nuclear nickel cluster in POM chemistry such as cross-type (Fig. 3a),⁴¹ S-shaped (Fig. 3b),⁴² hexagonal ring (Fig. 3c),⁴³ plane triangle (Fig. 3d)³⁶ and Z type {Ni₆} cluster (Fig. 3e).⁴⁴ Therefore, **2** represents an important new member of hexa-nuclear nickel cluster incorporated TMSPs.

3.3 The calculation of the bandgaps

The bandgaps (E_g) of **1** and **2** were calculated by UV-vis diffuse reflection measurements and the Tauc plots of $(\alpha h\nu)^{1/2}$. The E_g values for **1** and **2** were 2.78 eV and 2.57 eV (Fig. S5, ESI†), respectively, suggesting that they are potential semiconductive

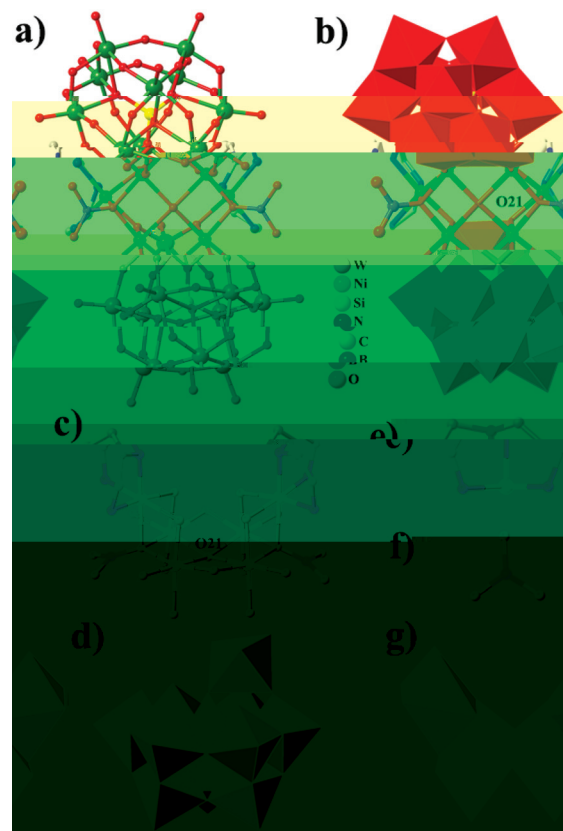


Fig. 2 (a) Ball-and-stick representation of **2**. (b) Combined polyhedral/ball-and-stick representation of compound **2**. (c) The {Ni₆} cluster. (d) The dilacunary Keggin polyanion {B-SiW₁₀}. (e) Coordination view of the Ni atom with dien. (f) The {BO₃} group. (g) The {Ni₆} polyhedron.

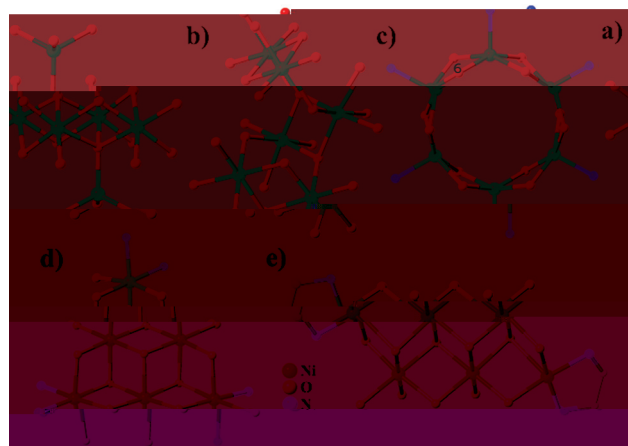


Fig. 3 (a) cross-type {Ni₆} cluster. (b) A894svispe el. (c) hexagonal ring {Ni₆} cluster. (d) plane triangle {Ni₆} cluster. (e) Z type {Ni₆} cluster.

materials. The photocatalytic activities of **1** and **2** were initially evaluated by a photocatalytic system of visible-light-driven CO₂ reduction with [Ru(bpy)₃]Cl₂·6H₂O and triethanolamine (TEOA) as the photosensitizer and the electron donor,

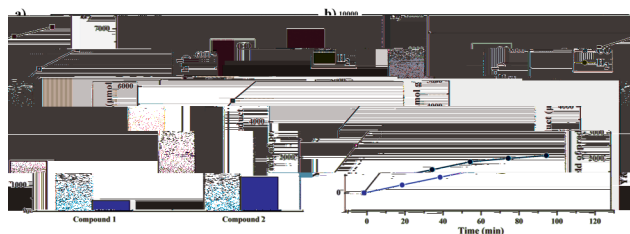


Fig. 4 (a) The yield of CO and H₂ of photoreduction using **1** and **2** as catalysts for 1 h. (b) The effect of the reaction time on the evolution of CO and H₂ from the CO₂ photoreduction. Reaction conditions: compounds (0.1 μmol), [Ru(bpy)₃]Cl₂·6H₂O (0.01 mmol) TEOA (1 mL), H₂O (1 mL) and acetonitrile (MeCN, 4 mL). The reaction setup was alternately vacuum degassed and purged with CO₂ three times, after which high-purity CO₂ was purged again for 30 min, λ ≥ 420 nm, 30 °C, 1 h.

respectively.^{45–47} The gas products of CO and H₂ were monitored by gas chromatography. Under continuously visible light irradiation, the production of CO and H₂ for **1** and **2** increased as time went by. The yields of CO and H₂ for **1** within 1 h irradiation were 1950 and 410 μmol g⁻¹ (TON = 23.71), respectively (Fig. 4a). Different from **1**, the yields of CO and H₂ for **2** within the same time reached to 6988 and 1315 μmol g⁻¹ (TON = 83.03), respectively, indicating that **2** is more active than **1** in photocatalytic reduction of CO₂ (Fig. 4a). Hence, the photocatalytic performance of **2** was further studied in detail in this work. As shown in Fig. 4b, the yield of CO increased at a constant speed in the first 40 min, but leveled off after 60 min.

The subsequent drop in performance may be due to the partial decomposition of [Ru(bpy)₃]Cl₂·6H₂O. To illuminate the origin of CO, an isotope tracer experiment involving ¹³CO₂ was carried out. The peaks at 2.7 min and the signal at $\lambda = 29$ were assigned to ¹³CO, demonstrating that CO originates from CO₂ reduction (Fig. S7, ESI†).

In order to further understand the role of components in photocatalytic system, a series of control experiments were performed (Table S6, ESI†). When the reactions were carried out in dark or nitrogen conditions, there was no CO or H₂ generated. When the experiments were conducted in the absence of photosensitizer or electron donor, the production was negligible, implying that [Ru(bpy)₃]Cl₂·6H₂O, TEOA are all indispensable for the reaction system. Without **2** as a catalyst, only a trace amount of CO and H₂ were detected, indicating that **2** plays an important role in photocatalytic system. In addition, when Ni(Ac)₂·4H₂O was used to replace **2** as a catalyst, there was no H₂ produced and only a few CO was detected (TON = 8.02). Meanwhile, the photocatalytic activity of the other reaction starting materials, such as Na₁₀[A-α-SiW₉O₃₄], were also explored, and there were only negligible CO/H₂ detected. UV-vis spectrum of **2** (1.7 × 10⁻⁵ M) was recorded in the solution with different aging time (0–10 h). The UV-vis curves of **2** remain unchanged during the aging course (Fig. S8, ESI†), which indicates the stability of **2** during the process of CO₂ photoreduction. The proposed mechanism of **2** in the photoreduction of CO₂ is presented in Fig. S9, ESI†. The [Ru(bpy)₃]²⁺ is excited from the ground state to the excited state under the

irradiation of visible light, and then, it interacts with TEOA to form the reductive photosensitizer. The reductive photosensitizer reverts to the ground state after transferring electrons to **2**. The process can effectively restrain the recombination of the electron-hole pair. Afterward, **2** provides active sites for CO₂ reduction. Ultimately, CO and H₂ are released from the system.^{25,27,45}

3.4 Magnetic properties

Variable-temperature magnetic susceptibilities of **1** and **2** were measured between 1.99 and 300 K with an applied magnetic field of 1000 Oe. As shown in Fig. 5, the χ_m value of **1** at 300 K is 16.89 cm³ K mol⁻¹. The value is slightly higher than the theoretical value of 12 cm³ K mol⁻¹ for twelve spin-only Ni²⁺ ions ($S = 1$ and $L = 2.0$), which is attributed to the strong orbital contribution of the high-spin octahedral Ni²⁺. The χ_m value declined gradually with the decreasing temperature and reached to a minimum of 12.91 cm³ K mol⁻¹ at 45 K. Below 45 K, the χ_m curve increased quickly to reach to a maximum of 16.04 cm³ K mol⁻¹ at about 6.44 K and then rapidly dropped to 14.84 cm³ K mol⁻¹ at 1.99 K. The decrease of χ_m value from room temperature might be associated with the characteristic spin-orbit coupling of the single Ni²⁺. Upon further cooling, the sharp upturn of χ_m reveals the presence of ferromagnetic interactions within the {Ni₁₂} spin core. Finally, the decrease of χ_m below 6.44 K is probably ascribed to the existence of magnetic anisotropy of Ni²⁺ ions (zero-field splitting of the ground state) or weak intramolecular antiferromagnetic interactions.^{48–50} Although possessing a simple Heisenberg model, it is also impossible to model the susceptibility due to the presence of different intramolecular magnetic interactions of the compound and the low symmetry of the Ni₁₂ center.⁵¹ Hence, it indicates that antiferromagnetic interactions should be in competition with ferromagnetic ones within the cores.

As shown in Fig. 6, the χ_m value of **2** at 300 K is 13.61 cm³ K mol⁻¹. This value is also slightly higher than the theoretical value of 12 cm³ K mol⁻¹ for twelve spin-only Ni^{II} ions ($S = 1$ and $L = 2.0$), which originated from the strong orbital contri-

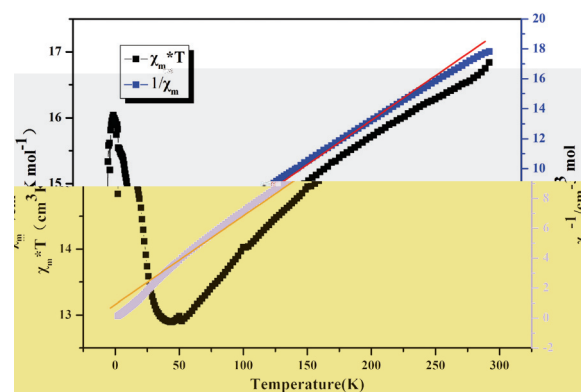


Fig. 5 The temperature dependence of $\chi_m T$ for **1** between 1.99 to 300 K.

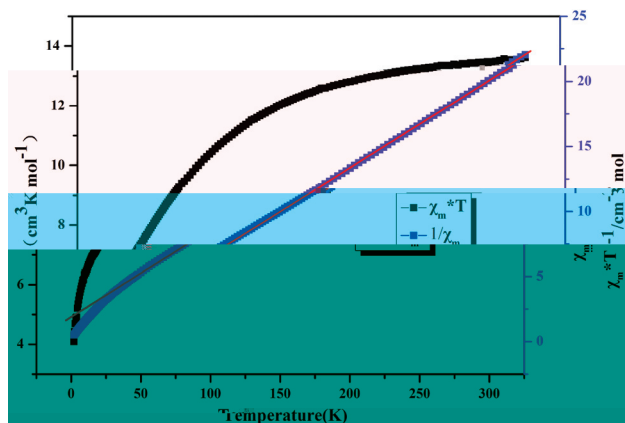


Fig. 6 The temperature dependence of $\chi_m T$ for **2** between 1.99 to 300 K.

bution of the high-spin octahedral Ni^{2+} . Upon further cooling, the χ_m product displayed a sustaining decrease smoothly from 300 K to a minimum of $4.09 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.99 K. This phenomenon shows that there are definitely antiferromagnetic interactions between the Ni^{2+} ions in **2**. Furthermore, alternating current magnetic susceptibilities of **1** and **2** with frequencies between 111 and 2311 Hz were collected under $H_{AC} = 3 \text{ Oe}$, and no frequency dependence was observed (Fig. S10 and S11, ESI†).

3.5 Proton conductivity

The presence of large amounts of Na^+ , delocalized H^+ , and H_2O molecules within **1** prompts us to evaluate its proton conduction performance. Firstly, the relative humidity (RH) dependence on **1** was measured in the range of 55–98% RH at 25°C . As shown in Fig. 7a, the conductivity (σ) increased from $3.74 \times 10^{-4} \text{ S cm}^{-1}$ to $7.33 \times 10^{-3} \text{ S cm}^{-1}$ when the RH increased from 55% to 98%, indicating the entry of more water into the structure as mobile proton transfer sites under high humidity conditions.^{52,53} Meanwhile, the temperature-dependence conduction behavior of **1** was tested between 25 and 50°C under 98% RH (Fig. 7b). The Nyquist plots reveal that the conductivity value shows a continuous increase and reaches to the maximum value of $1.89 \times 10^{-2} \text{ S cm}^{-1}$ at 98% RH as the temperature rises to 50°C , indicating that the temperature is more effective than RH in promoting the conductivity. The enhancement of the conductivity as the temperature rises should be attributed to the accelerated transfer of protons in the channel as the temperature increases. The conductivity of **1** at 50°C under 98% RH is comparable to some reported POM-based proton conductive materials.^{54–56} Finally, according to Arrhenius formula ($\sigma = \sigma_0 \exp(-E_a/RT)$), the activation energy of 0.33 eV was estimated by linear regression analysis, indicating that it belongs to the Grotthuss mechanism ($<0.4 \text{ eV}$) (Fig. 7c).⁵⁷ The PXRD characterization confirms that the structure of **1** remains intact after proton conductivity experiments (Fig. 7d).

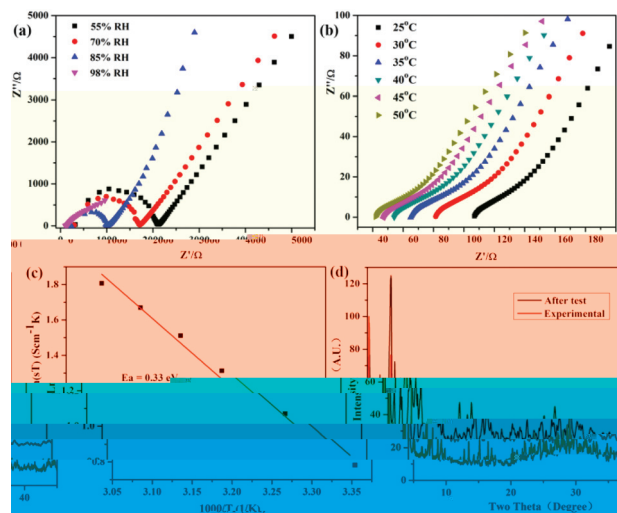


Fig. 7 (a) Nyquist plots for **1** at different RHs and $T = 25^\circ\text{C}$. (b) Nyquist plots for **1** at different temperatures and 98% RH. (c) Arrhenius plots of the conductivity of **1**. (d) The PXRD patterns of the as-synthesized sample and the sample after proton conductivity test for **1**.

4. Conclusions

In summary, two novel nickel cluster substituted POMs have been successfully synthesized and fully characterized. Interestingly, **1** is a novel Ni_{12} -substituted POM, in which a brand-new $\{\text{A-P}_2\text{Si}_2\text{W}_{22}\}$ fragment is found for the first time. And **2** is an uncommon sandwich-type TMSP structure with a boat-like Ni_6 core. CO_2 photoreduction experiments reveal that **2** exhibits a moderate catalytic activity. Moreover, the proton conduction experiments suggest that **1** may be a potential proton conduction material. This work not only enriches the structural diversity of nickel cluster substituted POM materials, but also extends the applications of TM cluster substituted POMs.

Conflicts of interest

The authors declare no conflicts of interest.

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