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Polyoxometalates

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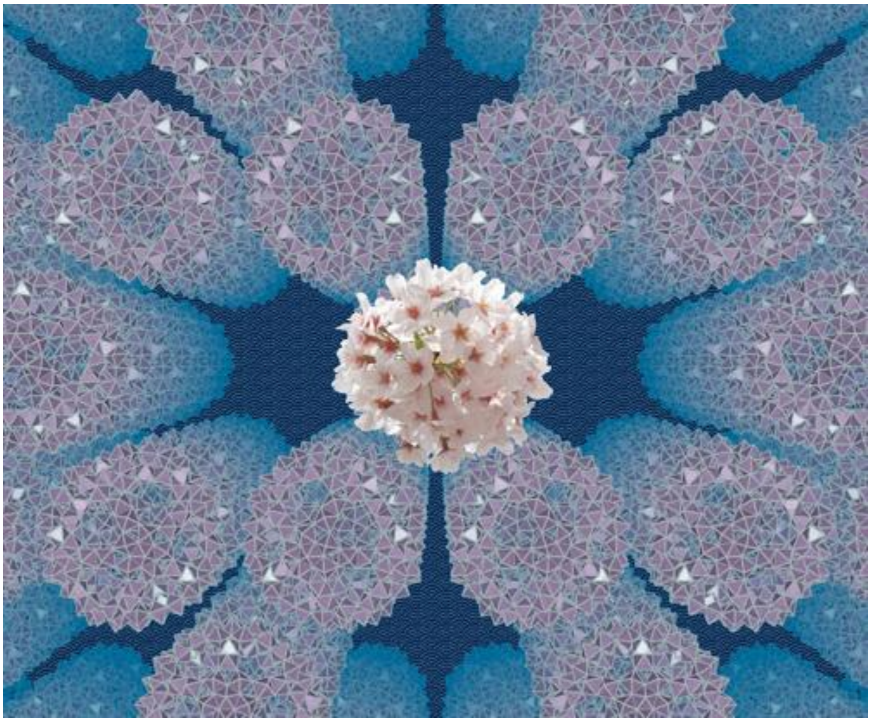

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Assembly of an undeca-nuclear nickel substituted POM through polycarboxylate ligand†

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An undeca-nuclear nickel substituted POM, namely $[Ni(H_2O)_6][Ni_{11}(PW_9O_{34})_2(IDA)_3(en)_2(Hen)_2(OH)_6]\cdot(H_2O)_7\cdot(H_2en)_2$ (1) (en = 1,2-ethylenediamine, H_2IDA = iminodiacetic acid), was synthesized through hydrothermal reaction of $Na_6PW_9O_{34}$, en, H_2IDA and $NiCl_2\cdot6H_2O$. Single-crystal structure reveals that 1 can be viewed as Ni_6PW_9 and Ni_5PW_9 units linked by a μ_3-O bridge and two IDA^{2-} ligands. Magnetic investigation indicates the presence of dominantly ferrimagnetic interactions within the Ni_{11} core. Electrochemistry study shows that 1 displays a stable and reproducible voltammetric graph.

Introduction

Polynuclear 3d transition-metal clusters have attracted considerable interest, due to their unique structures and potential applications in catalysis, magnetism and electrochemistry.[1] Polyoxometalates (POMs), featuring enriched oxygen atoms on their surface, are regarded as excellent inorganic multidentate O-donor ligands to construct polynuclear 3d transition-metal substituted POMs.[2] Compared with organic ligands, POMs possess their own structural features in size, shape and symmetry, which often lead to their playing different structure-directing roles in the formation of polynuclear metal clusters. Although a lot of polynuclear 3d transition-metal substituted POMs with unique structures and interesting properties have been synthesized,[3–8] most of them are constructed either through POMs or POMs and neutral organic ligands, those constructed from both POMs and polycarboxylate remain rare.[9,10]

Amino acids, such as, glycine and iminodiacetic acid (H_2IDA), have been proved to be excellent ligands in the construction of metal clusters.[11,12] More significantly, introducing these ligands into the transition-metal substituted POMs would favor increasing the number of metal ions in the 3d transition-metal substituted POMs, since they are negatively charged ligands. Accordingly, we, in this work, use iminodiacetic acid or 1-piperidine acid, $NiCl_2\cdot6H_2O$, 1,2-ethylenediamine, and $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot nH_2O$ (namely PW_9) to synthesize metal cluster substituted POMs and report herein crystal structures, magnetic and electrochemical properties of three nickel substituted POMs, namely $[Ni(H_2O)_6][Ni_{11}(PW_9O_{34})_2(IDA)_3(en)_2(Hen)_2(OH)_6]\cdot(H_2O)_7\cdot(H_2en)_2$ (**1**) (H_2IDA = iminodiacetic acid, en = 1,2-ethylenediamine).

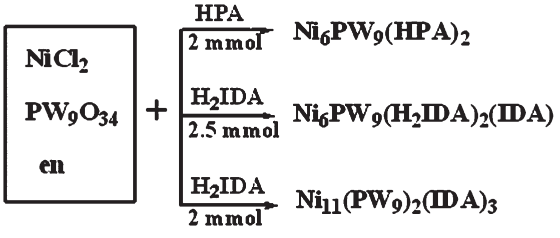
Experimental section

Materials and general methods

All solvents and starting materials for the synthesis were purchased commercially and were used as received. Infrared spectra were obtained in KBr discs on a Nicolet AVATAR FT-IR360 spectrometer in the range of 4000–400 cm^{-1} region. Elemental analyses of C, H and N were performed on a elementar Vario ELIII Elemental Analyzer. Elemental analyses of P, W and Ni were determined with a $GP_{3.5}$ -D1 ICP-AES. Thermogravimetric analyses (TGA) were carried out in a oxygen stream using SDT-Q600 TG/DTA equipment with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) data were recorded on a X'pert PRO X-ray powder diffractometer (CuKα, λ = 0.1504 nm) at room temperature. Electronic absorption spectra were recorded on a CHI 631B electrochemical workstation at room temperature under a nitrogen atmosphere.

$Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot nH_2O$ (PW_9) were prepared by a literature method (*Inorganic Syntheses*, John Wiley & Sons, New York, 1990, vol. 27, p. 85). The syntheses of compounds **1** to **3** are shown in Scheme 1.

Synthesis of $[Ni(H_2O)_6][Ni_{11}(PW_9O_{34})_2(IDA)_3(en)_2(Hen)_2(OH)_6]\cdot(H_2O)_7\cdot(H_2en)_2$ (1). PW_9 (0.30 g, 0.11 mmol),



Scheme 1 The simple synthetic chart for **1** to **3**.

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† Electronic supplementary information (ESI) available: X-ray crystallographic files in cif format, the stacking picture, selected bond distances and the XRD in figure format for **1**, **2** and **3**. CCDC reference numbers 861305–861307. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12507b

$NiCl_2 \cdot 6H_2O$ (0.80 g, 3.5 mmol), H_2IDA (0.266 g, 2.0 mmol) and en (0.3 mL) were mixed in 10.0 mL 0.5 M NaAc with stirring at room temperature. After stirring for about 30 min, the solution was transferred and sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 170 °C and held at that temperature for 5 days, then cooled to 100 °C at a rate of 4 °C h^{-1}. After 17 h, the solution was cooled to room temperature with a rate of 4 °C h^{-1}. Green plate crystals **1** (142.3 mg) were collected by filtration in 39.7% yield (based on $Na_9PW_9O_{34}$). Anal. Calcd (Found) for **1**: Ni, 11.25 (11.09); W, 52.85 (52.82); P, 0.99 (0.91); C, 4.60 (4.75); H, 1.66 (1.87); N: 3.36 (3.49). IR Spectra for **1** (KBr, cm^{-1}): 3432s, 2950w, 1635s, 1586m, 1544m, 1460w, 1388w,1034s, 941s, 849s, 798s, 719m, 510m.

Synthesis of $[Ni_6PW_9O_{34}(HPA)_2(OH)_3(en)_3(H_2O)_2]\cdot(H_2O)_{13}$ (2). Compound **2** was prepared in the same way as for **1**, except that the H_2IDA (2.0 mmol) was replaced with HPA (2.0 mmol). Green plate crystals **2** (104.5 mg) were collected by filtration in 28.0% yield (based on $Na_9PW_9O_{34}$). Anal. Calcd (Found) for **2**: Ni, 10.54 (10.53); W, 49.51 (51.23); P, 0.93 (0.91); C, 6.47 (6.51); H, 2.38 (2.19); N, 3.35 (3.39). IR Spectra for **2** (KBr, cm^{-1}): 3437s, 2950w, 1644s, 1452w, 1378w, 879m, 783s, 713s, 604m, 489m.

Synthesis of $[Ni_6PW_9O_{34}(H_2IDA)_2(HIDA)(OH)_3(Hen)_3]\cdot Cl_2\cdot(H_2O)_{11}$ (3). Compound **3** was prepared in the same way as for **1**, except that 2.5 mmol H_2IDA was used in the reaction. Green tetrahedral crystals **3** (98.1 mg) were collected by filtration in 25.0% yield (based on $Na_9PW_9O_{34}$). Anal. Calcd (Found) for **3**: Ni, 10.21 (10.23); W, 48.53 (48.93); P, 0.90 (0.94); C, 6.21 (6.30); H, 2.03 (1.82); N, 3.62 (3.65). IR Spectra for **3** (KBr, cm^{-1}): 3437s, 2948w, 1618s, 1456w, 1388w, 1041s, 950s, 868m, 780s, 708s, 500m.

Crystallography. Data collections were performed on a Rigaku R-AXIS RAPID IP diffractometer at 173 K for **1** and **2** on an Oxford Gemini S Ultra CCD area detector at 173 K for **3**. Absorption corrections were applied by using the analytical program Tompa-analytical for **1** and **2**, and multiscan program CrysAlis Red for **3**. The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program.[13] The SQUEEZE program was used to squeeze out the disordered solvent molecules for **1** and **2**, and part of the disordered water molecules for **3**.[13] The hydrogen atoms of organic ligands were generated geometrically (C–H, 0.96 Å; N–H, 0.90 Å). Crystal data as well as details of the data collection and refinement for the compounds are summarized in Table 1. Selected bond distances for the compounds are shown in Section S2 (ESI†)

Results and discussion

Single-crystal structural analysis reveals that **1** crystallizes in the space group *C*2/*m*. The asymmetric unit in the core of the cluster in **1** contains half a Ni_6PW_9 and Ni_5PW_9 units. The structure of the cluster in **1** can be viewed as Ni_6PW_9 and Ni_5PW_9 units linked by a μ_3-O bridge and two IDA^{2-} ligands as shown in Fig. 1. Structurally, the Ni_6PW_9 unit is similar to that reported by Yang and coworkers,[7b] that is, the six Ni^{2+} ions are arranged in an equilateral triangle with three on the vertex of the triangle and the remaining in the middle of the edge. However, there are differences between **1** and Yang's compounds. In **1**, each Ni^{2+} ion on the vertex is chelated with an IDA^{2-} ligand, while two Ni^{2+} ions in the middle of the edges are respectively coordinated to a Hen^+ ion, and the third Ni^{2+} on the middle of the edge is coordinated with a μ_3-O bridge linked to the Ni_5PW_9 unit. In contrast, the Ni_5PW_9 unit has not been reported yet. The five Ni^{2+} ions in the Ni_5PW_9 unit are arranged in an isosceles trapezoid with four Ni^{2+} ions on the vertex of the isosceles trapezoid and one Ni^{2+} ion in the middle of the longer edge in the isosceles trapezoid. Each Ni^{2+} ion in the shorter edge of the isosceles trapezoid, locating in octahedron geometry, is coordinated by one mondentate carboxylate oxygen atom from IDA^{2-} ligand, two μ_2-O from PW_9, two μ_3-O from the PW_9 and one water molecule respectively. Of the three Ni^{2+} in the longer edge, two on the vertex are coordinated by two nitrogen atoms from one en, one oxygen atom from IDA^{2-} ligand, two μ_2-O and one μ_3-O from the PW_9, one in the middle of the longer edge in the isosceles trapezoid is coordinated by one terminal H_2O, two μ_2-O and three μ_3-O respectively from the PW_9. It was mentioned that **1** is the third example of nickel substituted POMs with the number of the nickel ions higher than 10 reported so far, the other two are $[Ni(enMe)_2]_3[H_6Ni_{20}P_4W_{34}(OH)_4O_{136}(enMe)_8(H_2O)_6]\cdot 12H_2O$[7a] and $[Ni_{12}(OH)_9WO_4(W_7O_{26}(OH))(PW_9O_{34})_3]^{25-}$[7c] respectively. The bond lengths in **1** are 1.66 (2)–2.515(14) Å for W–O and 1.46 (2)–1.58(2) Å for P–O, comparable to those of 1.692–2.526 Å for W–O and 1.528–1.558 Å for P–O in nickel substituted POMs Ni_{20}[7a] and Ni_{12}.[7c] The bond lengths of Ni–O, Ni–N in **1** are 1.96(2)–2.25(3) and 2.027(16)–2.23(3) Å respectively, slightly longer than those in nickel substituted POMs Ni_{20}[7a] and Ni_{12},[7c] but comparable to those in the organic ligand-based Ni-clusters of Ni_{11}[14a] and Ni_{14}.[14b] The separations of Ni···Ni are 2.992 to 3.614 Å, longer than those in Ni_6PW_9 reported previously.[7b]

In order to confirm that it is the IDA^{2-} ligand that plays a key contribution in the formation of **1**, HPA ligand was used to synthesize transition-metal substituted POMs under similar synthetic conditions as described for **1**. In this case, compound **2** $[Ni_6PW_9O_{34}(HPA)_2(OH)_3(en)_3(H_2O)_2]\cdot(H_2O)_{13}$ was obtained. Single-crystal structural analysis reveals that **2** crystallizes in the space group *Pna*2$_1$. As shown in Fig. 2a, the six Ni^{2+} ions were arranged in an equilateral triangle with three Ni^{2+} ions on the vertex of the triangle and the remaining in the middle of the edge of the equilateral triangle, similar to that reported by Yang and co-workers.[7b] Of the three Ni^{2+} ions in the vertex in **2**, one is coordinated by two nitrogen atoms from one en ligand and four oxygen atoms with one from water and three from PW_9, the other two are coordinated by two nitrogen atoms from one en ligand and four oxygen atoms with one from the carboxylate of HPA and three from PW_9 respectively. Of the three Ni^{2+} ions in the middle of the edge, one is coordinated by six oxygen atoms with five from PW_9 and one from a terminal aqua ligand, the other two are coordinated by six oxygen atoms with five from PW_9 and one from the carboxylate of the HPA ligand. The bond lengths of Ni–O, Ni–N, W–O and P–O are 1.992(7)–2.304(8), 2.018(11)–2091(8), 1.689(9)–2.504(8), and 1.500(9)–1.570(7) Å respectively, comparable to those in the nickel substituted POMs Ni_{20}[7a] and Ni_{12}.[7c] The separations of Ni···Ni are 2.968 to

Table 1 Crystal data and details of the data collection and refinement for compounds **1** to **3**

Complex	**1**	**2**	**3**
Formula	$C_{24}H_{103}O_{99}N_{15}P_2W_{18}Ni_{12}$	$C_{18}H_{79}O_{56}N_8PW_9Ni_6$	$C_{18}H_{70}O_{60}N_9Cl_2PW_9Ni_6$
M_r	6261.97	3341.56	3481.61
T/K	173(2)	173(2)	173(2)
Cryst syst	Monoclinic	Orthorhombic	Orthorhombic
Space group	$C2/m$	$Pna2_1$	$Cmc2_1$
a/Å	38.794(8)	22.325(5)	19.698(5)
b/Å	20.940(4)	20.827(4)	19.032(5)
c/Å	17.201(3)	13.671(3)	20.289(5)
β (°)	105.63(3)	90	90
V/Å^3	13 457(5)	6357(2)	7606.1(3)
Z	4	4	4
D_c/g cm^{-3}	3.091	3.492	3.040
μ/mm^{-1}	17.071	18.089	15.196
Data/params	13 580/743	12 083/766	6370/467
θ (°)	3.09–26.00	3.06–26.00	2.93–26.00
Obsd reflns	8498	10 988	5712
R_1 $[I > 2\sigma(I)]^a$	0.0885	0.0596	0.0456
wR_2 (all data)^b	0.2516	0.1519	0.0943

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

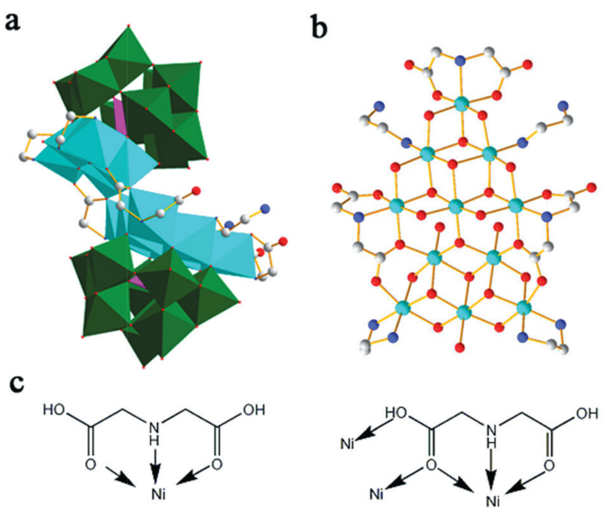

Fig. 1 (a) Structure of $[Ni_{11}(PW_9)_2(IDA)_3(en)_2(Hen)_2(OH)_6]^{6-}$ in **1**. (b) Ball-and-stick representation of $[Ni_{11}(IDA)_3(en)_2(Hen)_2(OH)_6]^{18+}$ in **1**. WO_6: green; PO_4: purple; NiO_6, NiO_5N and NiO_4N_2: cyan, Ni: cyan, O: red, N: blue, C: gray. Hydrogen atoms are omitted for clarity. (c) Coordination modes of H_2IDA ligand in **1**.

3.169 Å, comparable to those in Ni_6PW_9 reported previously.[7b] Owing to the very similar synthetic conditions for **1** and **2**, the structural differences between **1** and **2** indicate that the IDA^{2-} ligand plays a key role in the formation of the cluster **1**.

It was mentioned that, although introducing IDA^{2-} ligand is of key importance for the formation of **1**, further investigation shows that the amount of IDA^{2-} ligand used in the synthesis is another important factor influencing the formation of **1**. When the amount of the IDA^{2-} ligand used in the synthesis is 2.5 mmol, instead of 2.0 mmol as described for **1**, compound **3** $[Ni_6PW_9O_{34}(H_2IDA)_2(HIDA)(OH)_3(Hen)_3]\cdot Cl_2\cdot(H_2O)_{11}$ was obtained. Single-crystal analysis reveals that **3** crystallizes in the space group $Cmc2_1$. The asymmetric unit in **3** contains half a Ni_6PW_9 and one $HIDA^-$ ligand and half a H_2IDA ligand. Structurally, the Ni_6 cluster in **3** is very similar to the Ni_6PW_9 unit of **1**, except the μ_3-O bridge linked to the Ni_5PW_9 in **1** is replaced by monodentate coordinated Hen^+ ligand as shown in Fig. 2b. The bond lengths of Ni–O, Ni–N, W–O and P–O are 1.962(8)–2.205(11), 2.032(16)–2.151(18), 1.693(8)–2.529(10), and 1.536(11)–1.562(8) Å respectively, are comparable to those in the nickel substituted POMs Ni_{20}[7a] and Ni_{12}.[7c] The separations of Ni⋯Ni are 3.068 to 3.166 Å, comparable to those in **2**.

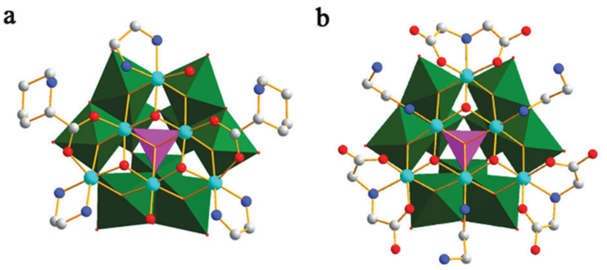

Fig. 2 (a) Structure of $[Ni_6PW_9(OH)_3(HPA)_2(en)_3]$ cluster in **2**; (b) structure $[Ni_6PW_9(H_2IDA)_2(HIDA)(OH)_3(Hen)_3]^{2+}$ in **3**. WO_6: green; PO_4: purple; Ni: cyan, O: red, N: blue, C: gray. Hydrogen atoms are omitted for clarity.

Thermal analysis

The TGA experiments were carried out for **1** to **3** in a flow of air with a heating rate of 10 °C min^{-1} from 30 °C to 800 °C (Fig. 3 (a)–(c)). For **1**, the weight loss in the temperature range from 30 °C to 200 °C corresponds to the removal of seven lattice water molecules and two lattice en molecules per formula unit (observed, 3.42%; calcd 3.86%). The remaining two stages (in the ranges 300 °C to 450 °C and 550 °C to 700 °C) are mainly attributed to the loss of the H_2IDA ligands, four en molecules, six coordinate water molecules and one P_2O_5 molecule per formula unit (observed, 14.03%; calcd 14.15%). Assuming that the residue corresponds to WO_3 and NiO, the observed

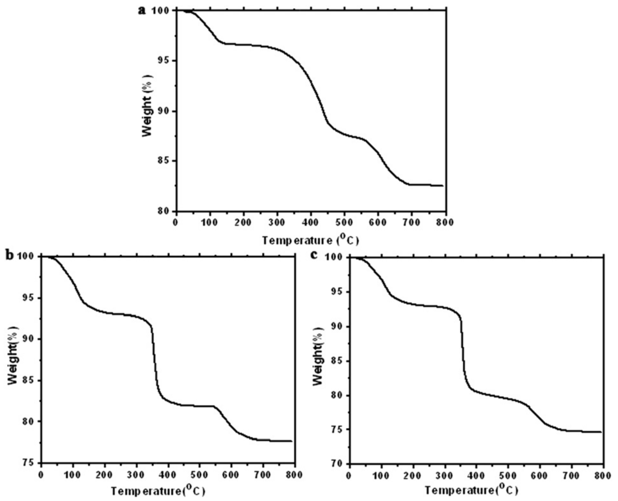

Fig. 3 TG curves from room temperature to 800 °C (a) for **1**, (b) for **2** and (c) for **3**.

residual weight 82.55% is in good agreement with the calculated value of 81.99%.

The TGA curves of **2** and **3** show similar weight loss processes to that of **1**. The weight loss (observed, 6.05% for **2**, 7.51% for **3**) from 30 °C to 200 °C corresponds to the removal of thirteen lattice water molecules for **2** (calcd 6.91%) and eleven lattice water and two hydrochloric acid molecules for **3** (calcd 7.78%). The second weight loss (observed, 11.46% for **2**, 13.25% for **3**) from 300 °C to 450 °C is assigned to the removal of two HPA ligands and three en molecules for **2** (calcd 11.32%), the removal of three H_2IDA ligands and three en molecule for **3** (calcd 13.79%). The third weight loss (observed, 4.79% for **2**, 5.23% for **3**) from 550 °C to 700 °C is mainly attributed to the loss of one P_2O_5 molecule and six water molecules from $Ni(OH)_2$ (calcd 5.35% for **2**, 5.22% for **3**). The observed residual weight of 77.70% for **2** and 74.01% for **3** is in agreement with the calculated value of 76.42% for **2** and 73.21% for **3** respectively.

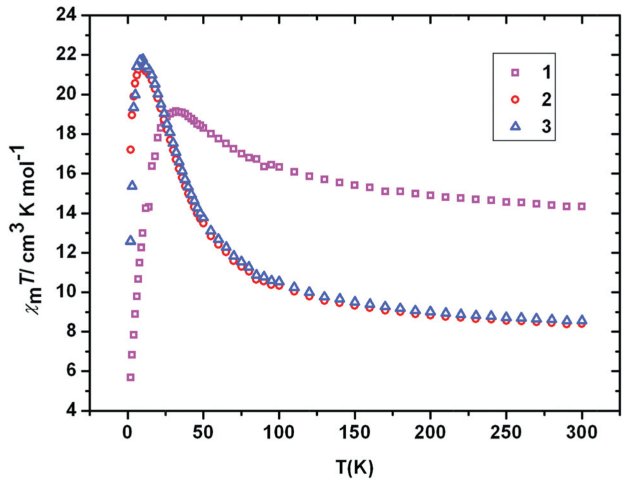

Fig. 4 Temperature dependence of the $\chi_M T$ at 1000 Oe, amaranth: **1**; red: **2**; and blue: **3**.

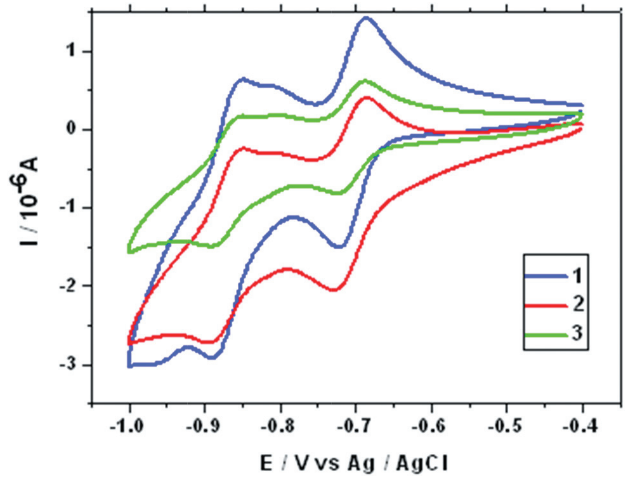

Fig. 5 Cyclic voltammograms of **1–3** in 2 × 10^{-4} M in pH = 4.3 (0.4 M CH_3COONa + CH_3COOH). The scan rate was 10 mV s^{-1}, the working electrode was GC, and the reference electrode was SCE. (**1**: blue; **2**: red; **3**: green).

Magnetic properties

The dc magnetic susceptibility for **1** to **3** was measured in the temperature range of 2.0 to 300 K under an applied magnetic field of 1000 Oe. The $\chi_M T$ *vs.* T plots are given in Fig. 4. The $\chi_M T$ products of **1**, **2** and **3** at room temperature is 14.31, 8.40 and 8.55 cm^3 mol^{-1} K per formula unit, respectively, which are expected for eleven, six and six uncoupled high-spin Ni^{2+} ion with $g > 2$.[7c] With the decrease of the temperature, the $\chi_M T$ values of **1** continuously increase and reach 19.1 cm^3 mol^{-1} K at 25 K, indicating that intramolecular ferrimagnetic interactions are dominant between Ni(II) centers in the Ni_{11} core. Below 25 K, the $\chi_M T$ values quickly drop to 5.7 cm^3 mol^{-1} K at 2.0 K, probably as a result of the presence of magnetic anisotropy (zero-field splitting of the ground state) or weak antiferromagnetic intra/inter-complex interactions. The magnetic susceptibility of **2** and **3** is similar to that reported by Yang and co-workers,[7b] indicating that intramolecular ferromagnetic interactions exist between Ni(II) centres in the Ni_6 core. The magnetic interactions in **1** are different from those in **2** and **3** which may be related to the longer Ni⋯Ni separations between the neighbour Ni^{2+} ions in **1** (separations of Ni⋯Ni are: 2.991(0) to 3.609 (1) Å in **1**, 2.974(0) to 3.170(1) Å in **2**, 3.070 to 3.167 Å in **3**).

Electrochemistry

Fig. 5 shows the typical cyclic voltammetric behavior of **1–3** in the pH = 4.3 (0.4 M CH_3COONa + CH_3COOH) buffer solution at different scan rates. Two quasireversible redox peaks (−0.721 V and −0.889 V for **1**, −0.725 V and −0.893 V for **2**, −0.723 V and −0.892 V for **3**) were respectively observed for the three compounds in the potential range from −0.4 to −1.0 V. The cyclic voltammograms of the three compounds are very similar in shape and are similar to the nickel substituted POMs.[7f,g] Based on the previous literature,[7f] the peak at about −0.72 V corresponds to the redox of the W^{VI} in the compounds **1** to **3**.

Conclusions

In conclusion, three nickel substituted POMs of $[Ni(H_2O)_6]$-$[Ni_{11}(PW_9O_{34})_2(IDA)_3(en)_2(Hen)_2(OH)_6]\cdot(H_2O)_7\cdot(H_2en)_2$, $[Ni_6PW_9O_{34}(HPA)_2(OH)_3(en)_3(H_2O)_2]\cdot(H_2O)_{13}$ and $[Ni_6PW_9O_{34}(H_2IDA)_2(HIDA)(OH)_3(Hen)_3]\cdot Cl_2\cdot(H_2O)_{11}$ have been prepared. Based on their structure and synthetic condition differences, we revealed that introducing the polycarboxylate ligand of IDA^{2-} into POMs would favor the formation of high-nuclearity nickel substituted POMs. Magnetic study shows that compound **1** exhibits dominantly ferrimagnetic interactions within Ni_{11} core, while compounds **2** and **3** show dominantly ferromagnetic interactions within the Ni_6 core. Thus, the present work provides a new synthetic route to high-nuclearity metal substituted POMs.

Acknowledgements

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