

基于 5-甲基-3-吡唑甲酸为配体的钴(II)、镍(II)配合物的合成、晶体结构和电化学性质

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摘要: 利用 5-甲基-3-吡唑甲酸、咪唑和相应醋酸盐在乙醇和水混合溶剂中反应, 得到了配合物 $[M(\text{MPA})_2(\text{Im})_2] \cdot 2\text{H}_2\text{O}$ (**1**: $M=\text{Co}$; **2**: $M=\text{Ni}$) (HMPA=5-甲基-3-吡唑甲酸, Im=咪唑)。用元素分析、红外光谱、X-单晶衍射结构分析、热重分析、循环伏安等对其进行了表征。配合物 **1** 和 **2** 的晶体结构参数如下: 配合物 **1** 和 **2** 的晶体都属于单斜晶系, 空间群为 $P2_1/n$ 。配合物 **1** 的晶胞参数为 $a=0.847\ 02(16)\text{ nm}$, $b=1.461\ 5(3)\text{ nm}$, $c=0.899\ 67(17)\text{ nm}$, $\beta=101.759(6)^\circ$, $V=1.090\ 3(4)\text{ nm}^3$, $Z=2$; 配合物 **2** 的晶胞参数为 $a=0.853\ 59(6)\text{ nm}$, $b=1.451\ 77(9)\text{ nm}$, $c=0.889\ 83(6)\text{ nm}$, $\beta=102.382\ 0(10)^\circ$, $V=1.077\ 04(12)\text{ nm}^3$, $Z=2$ 。金属离子与来自 2 个 5-甲基-3-吡唑甲酸配体中的 2 个氮原子及 2 个氧原子, 2 个咪唑分子中的 2 个氮原子配位, 形成八面体配位构型。配合物中的独立结构单元 $[M(\text{MPA})_2(\text{Im})_2] \cdot 2\text{H}_2\text{O}$ 通过 2 种分子间氢键($\text{N}-\text{H}\cdots\text{O}$ 和 $\text{C}-\text{H}\cdots\text{O}$) 形成三维超分子。循环伏安性质测试表明配合物 **1** 和 **2** 的电解过程均为可逆过程。

关键词: 钴; 镍; 5-甲基-3-吡唑甲酸; 晶体结构; 电化学性质

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Syntheses, Crystal Structures and Electrochemical Properties of Cobalt and Nickel Complexes Based on 5-Methyl-1H-pyrazole-3-carboxylic Acid Ligand

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Abstract: The new monomeric complexes of $[M(\text{MPA})_2(\text{Im})_2] \cdot 2\text{H}_2\text{O}$ (**1**: $M=\text{Co}$; **2**: $M=\text{Ni}$) (HMPA=5-methyl-1H-pyrazole-3-carboxylic acid, Im=imidazole) were synthesized by the reaction of HMPA and Im with $M(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ($M=\text{Co}, \text{Ni}$), respectively. The compounds were characterized by elemental analysis, IR spectra, single crystal X-ray diffraction, thermogravimetric analysis and cyclic voltammetry. The structural parameters of **1** and **2** were analyzed as follows: **1**, monoclinic, $P2_1/n$, $a=0.847\ 02(16)\text{ nm}$, $b=1.461\ 5(3)\text{ nm}$, $c=0.899\ 67(17)\text{ nm}$, $\beta=101.759(6)^\circ$, $V=1.090\ 3(4)\text{ nm}^3$, $Z=2$; **2**, monoclinic, $P2_1/n$, $a=0.853\ 59(6)\text{ nm}$, $b=1.451\ 77(9)\text{ nm}$, $c=0.889\ 83(6)\text{ nm}$, $\beta=102.382\ 0(10)^\circ$, $V=1.077\ 04(12)\text{ nm}^3$, $Z=2$. Metal ions have all octahedral geometry coordinated by two nitrogen atoms from two Im molecules, two nitrogen atoms and two oxygen atoms from two MPA^- ligands. In both complexes, the independent components $[M(\text{MPA})_2(\text{Im})_2] \cdot 2\text{H}_2\text{O}$ are connected by two kinds of intermolecular hydrogen bonds ($\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$) to form a three-dimensional supramolecular architecture. Electrochemical property of the complex shows that electron transfer of $M(\text{II})$ between $M(\text{III})$ ($M=\text{Co}, \text{Ni}$) in electrolysis is quasi-reversible process. CCDC: 848231, **1**; 848232, **2**.

Key words: cobalt(II); nickel(II); 5-methyl-1H-pyrazole-3-carboxylic acid; crystal structure; electrochemical property

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0 Introduction

Currently, much attention has been paid to the metal-organic supramolecular complexes assembled by coordinate bond and/or hydrogen bond, due to their potential applications in separation, catalysis, molecular recognition, gas storage, chemical sensor, biometric activity and so forth^[1-5]. In particular, supramolecular complexes formed through hydrogen bond have attracted great attention owing to their special structures and properties. Accordingly, in order to design and construct the well-regulated supramolecular architectures with new functions, we should be able to employ appropriate bridging ligands and choose suitable metal ions. The organic bridging ligands containing heterocyclic nitrogen and carboxyl oxygen atoms, such as imidazolecarboxylic acid^[6], pyrimidinecarboxylic acid^[7-9], pyrazinecarboxylic acid^[10-11], pyridinecarboxylic acid^[12-13], pyrazolecarboxylic acid^[14-23] and so forth, which are versatile ligands due to their multi-coordination modes by the N and O donor atoms, have been chosen to use in synthesizing supramolecular complexes with various functional properties. Similarly to the organic ligands mentioned above, 5-methyl-1*H*-pyrazole-3-carboxylic acid (HMPA), can also use its carboxylate oxygen and pyrazole nitrogen atoms, which are highly accessible to metals, to form monodentate or multidentate M-O and M-N bonds; besides, it can also act as a donor and / or acceptor in hydrogen bond interactions. However, the studies of constructing the supramolecular complexes using HMPA are very rare^[24-25]. On the other hand, imidazole (Im), as a good organic ligand and donor / acceptor of hydrogen bond, has been employed to react with metal salts to form complexes with novel structures^[26-29], many imidazole derivatives possess various pharmacological effects, containing antiinflammatory, antimicrobial and antitumor activities, have been documented^[30]. But, to the best of our knowledge, the supramolecular compounds containing HMPA and Im have not been reported so far. As the continuing of our work in constructing new functional supramolecular complexes, we studied the reactions of $M(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$

($M=\text{Co}, \text{Ni}$), HMPA and Im. In this paper, we report the synthesis, crystal structures of two new three-dimensional supramolecular complexes: $[\text{M}(\text{MPA})_2(\text{Im})_2] \cdot 2\text{H}_2\text{O}$ (**1**: $M=\text{Co}$; **2**: $M=\text{Ni}$). In addition, IR spectra, thermal decomposition and electrochemical properties will be discussed.

1 Experimental

1.1 Materials and methods

All solvents and starting materials for synthesis were purchased commercially and were used as received unless otherwise noted. 5-methyl-1*H*-pyrazole-3-carboxylic acid (HMPA) was synthesized and purified according to the modified literature method^[31]. The elemental analysis (C, H and N) was performed on a Perkin-Elmer 2400 Series II element analyzer. FTIR spectra were recorded on a Nicolet 460 spectrophotometer in the form of KBr pellets. Single-crystal X-ray diffraction measurement of the title compounds were carried out with a Bruker Smart Apex II CCD diffractometer at 296(2) K. Thermogravimetric analysis (TGA) experiments were carried out on a Dupont thermal analyzer with a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ under N_2 atmosphere. The cyclic voltammogram experiments were carried out on a microcomputer-based electrochemical analyzer (Tianjin Lanlike Chemical and Electron High Technology Co. Ltd) in highly pure nitrogen atmosphere. A Pt-piece was employed as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as auxiliary electrode. The supporting electrolyte was $0.1\text{ mol} \cdot \text{L}^{-1}$ NaCl. The half wave potentials $E_{1/2}$ were obtained from $(E_{\text{pa}} + E_{\text{pc}})/2$.

1.2 Synthesis

1.2.1 Preparation of **1**

To a solution containing HMPA (0.012 6 g, 0.1 mmol) and Im (0.017 0 g, 0.25 mmol) in EtOH (7 mL) was added a solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.024 9 g, 0.1 mmol) in water (3 mL). The resulting solution was stirred for one hour and allowed to stand at room temperature for a week. Red block crystals of **1** suitable for X-ray diffraction analysis were obtained. Anal. Calcd. for $\text{C}_{16}\text{H}_{22}\text{CoN}_8\text{O}_6$ (%): C 39.89; H 4.57; N

23.27. Found (%): C 39.75; H 4.69; N 22.54. IR spectrum (cm^{-1} , KBr pellet): 3 362(m), 3 139(m), 3 095(w), 2 929(w), 2 855(w), 2 243(w), 1 602(vs), 15 35(s), 1 498(m), 1 425(s), 1 380(w), 1 350(s), 1 332(w), 1 292(s), 1 261(w), 1 218(m), 1 186(w), 1 141(m), 1 097(m), 1 075(s), 1 017(s), 941(m), 888(m), 848(m), 833(m), 795(m), 742(m), 713(w), 664(s), 636(w), 619(w), 593(w), 558(m), 449(m).

1.2.2 Preparation of **2**

The blue block single crystals of **2** suitable for X-ray analysis were obtained by adopting the procedure similar to **1**, only using Ni (OAc)₂·4H₂O (0.024 9 g, 0.1 mmol) instead of Co (OAc)₂·4H₂O (0.024 9 g, 0.1 mmol). Blue block crystals of **2** suitable for X-ray diffraction analysis were obtained. Anal. Calcd. for C₁₆H₂₂NiN₈O₆ (%): C 40.07; H 4.17; N 23.38. Found (%): C 39.85; H 4.47; N 22.75. IR spectrum (cm^{-1} , KBr pellet): 3 345(m), 3 167(w), 3 139(m), 2 959(m), 2 857(m), 2 259(w), 1 602(vs), 1 538(s), 1 499(s), 1 428(vs), 1 382(m), 1 353(s), 1 334(m), 1 296(s), 1 263(m), 1 223(s), 1 185(m), 1 145(m), 1 098(m), 1 077(s), 1 047(w), 1023(s), 1016(w), 941(s), 898(m), 844(m), 822(w), 795(m), 741(m), 665(s), 655(w), 619(m), 603

(w), 561(m), 453(m).

1 and **2** are stable in air (via IR spectra analysis and elemental analysis), soluble in H₂O, C₂H₅OH, CH₃CN, DMF, insoluble in ether.

1.3 X-ray crystallography

Single-crystal X-ray diffraction measurement of **1** and **2** were carried out with a Bruker Smart Apex II CCD diffractometer at 296(2) K. Intensities of reflections were measured using graphite-monochromatized Mo K α radiation ($\lambda=0.071\ 073\ \text{nm}$) with the φ - ω scans mode in the range of $2.70^\circ \leq \theta \leq 25.00^\circ$ (for **1**) and $2.73^\circ \leq \theta \leq 27.46^\circ$ (for **2**). The structures were solved by direct methods using SHELXS-97^[32] computer program and refined by full-matrix least-squares methods on F^2 with the SHELXL-97 program package. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. Hydrogen atoms were included in calculated position and refined with isotropic thermal parameters riding on the parent atoms. H atoms bonded to O or N were located in difference Fourier maps. Crystallographic data parameters for structural analyses are summarized in Table 1.

CCDC: 848231, **1**; 848232, **2**.

Table 1 Crystal structure parameters of the title complexes

Compound	1	2
Empirical formula	C ₁₆ H ₂₂ CoN ₈ O ₆	C ₁₆ H ₂₂ NiN ₈ O ₆
Formula mass	481.35	481.13
Color	Orange	Blue
Crystal size / mm	0.30×0.22×0.20	0.20×0.20×0.18
Temperature / K	296(2)	296(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a / nm	0.846 70(7)	0.853 59(6)
b / nm	1.460 95(11)	1.451 77(9)
c / nm	0.899 05(7)	0.889 83(6)
β / (°)	101.766(2)	102.382 0(10)
V / nm ³	1.088 75(15)	1.077 04(12)
Z	2	2
D_c / (g·cm ⁻³)	1.468	1.484
μ (Mo K α) / mm ⁻¹	0.838	0.951
Index ranges (h, k, l)	-9 / 10, -15 / 17, -10 / 10	-6 / 11, -17 / 18, -11 / 11
$F(000)$	498	500
θ range for data collection / (°)	2.70 to 25.00	2.73 to 27.46

Continued Table 1

Reflections collected	5 882	7 061
Independent reflections (R_{int})	1 908 (0.030 5)	2 436 (0.078 4)
Observed reflections	1 723	1 987
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1 908 / 3 / 143	2 436 / 2 / 149
Goodness-of-fit on F^2	1.170	1.092
R_1, wR_2 ($I > 2\sigma(I)$)	0.028 1, 0.087 8	0.033 0, 0.082 5
R_1, wR_2 (all data)	0.041 0, 0.110 4	0.044 4, 0.099 3
Largest diff. peak and hole / ($e \cdot nm^{-3}$)	450, -450	760, -520

2 Results and discussion

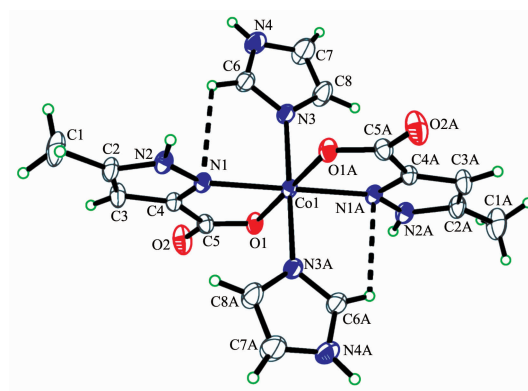
2.1 IR spectra

The IR spectrum of **1** and **2** are similar, the strong and broad absorption bands around 3 000~3 500 cm^{-1} region in **1** and **2** are assigned as characteristic peaks of OH vibration, indicating that water molecules exist in both of them. Moreover, the strong peaks appearing at 1 535 cm^{-1} in **1** and 1 538 cm^{-1} in **2** are attributed to the stretching vibrations of C=N. The absorption peak between 1 690 and 1 730 cm^{-1} is not observed, showing all carboxylic groups are deprotonated in **1** and **2**. For **1**, the strong peaks at 1 602 and 1 380 cm^{-1} are the $\nu_{as}(COO^-)$, and $\nu_s(COO^-)$ stretching mode of the coordinated MPA⁻ ligand, respectively, while for **2**, the peaks at 1 613 and 1 382 cm^{-1} belong to the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ respectively. The different values between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ of **1** and **2** are 222 and 231 cm^{-1} respectively, which indicate that MPA⁻ ligand adopt monodentate coordination^[33-35] as proved by the X-ray crystal structure analysis of them.

2.2 Structural description of **1** and **2**

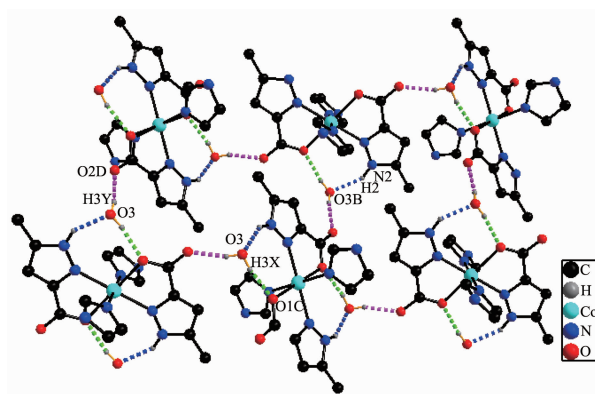
The crystal structures of **1** and **2** are isostructural (Fig.1, 2 and 3 show the structure of **1**). As shown in Fig.1, the coordination sphere of each metal ion is defined by O1A, O1, N1A and N1 atoms from the two MPA⁻ ligands as well as its adjacent N3A and N3 atoms from the two Im molecules, leading to an octahedral geometry. O1A, O1, N3A and N3 atoms from two MPA⁻ ligands and Im respectively form the equator plane of the octahedron, while the remaining two apical positions are occupied by two nitrogen atoms from the two MPA⁻ ligands respectively.

Selected bond lengths and angles for **1** and **2** are



Symmetry code: A: 1-x, -y, 1-z

Fig.1 Molecular structure of complex **1** with thermal ellipsoid at 30% probability level



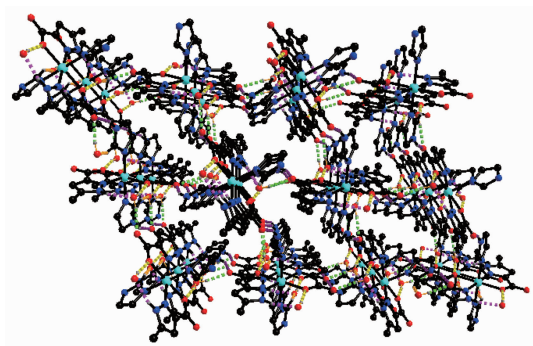
Symmetry codes: B: 3/2-x, -1/2+y, 3/2-z; C: 1/2+x, 1/2-y, 1/2+z; D: 1/2+x, 1/2-y, -1/2+z

Fig.2 Hydrogen bonding interactions in complex **1**

given in Table 2. The average bond length of Co-N 0.212 3(2) nm is longer than that of Co-O 0.211 8(2) nm, showing that the strength of cobalt ion coordinated with nitrogen atoms are weaker than that of oxygen atoms from MPA⁻ ligand in **1**; while opposite case is observed in **2** [Ni-N 0.2078(2) nm, Ni-O 0.209 9(2) nm]. The bond angles of N3-Co1-O1, N3-Co1-O1A, O1A-Co1-N3A, N3A-Co1-O1 are add up to equal to 360°,

Table 2 Selected bond lengths (nm) and angles (°) for complex **1** and **2**

Complex 1					
Co1-N3	0.212 10(18)	Co1-N1	0.212 26(16)	Co1-O1	0.211 74(15)
Co1-N3A	0.212 10(18)	Co1-N1A	0.212 26(16)	Co1-O1A	0.211 74(15)
N3A-Co1-N3	180.0	N1A-Co1-N1	180.0	O1-Co1-N1	76.98(6)
O1-Co1-N3A	91.36(7)	O1-Co1-N1A	103.02(6)	O1A-Co1-N1	103.02(6)
O1A-Co1-N3A	88.64(7)	O1A-Co1-N1A	76.98(6)	N3A-Co1-N1	90.66(7)
O1-Co1-N3	88.64(7)	N3A-Co1-N1A	89.34(7)	N3-Co1-N1	89.34(7)
O1A-Co1-N3	91.36(7)	N3-Co1-N1A	90.66(7)	O1-Co1-O1A	180.0
Complex 2					
Ni1-N1	0.206 82(14)	Ni1-N3	0.20856(15)	Ni1-O1	0.209 80(13)
Ni1-N1A	0.206 82(14)	Ni1-N3A	0.208 56(15)	Ni1-O1A	0.209 80(13)
N1A-Ni1-N1	180.0	N3A-Ni1-N3	180.0	N1A-Ni1-O1	101.75(5)
N1A-Ni1-N3A	89.35(6)	N1A-Ni1-O1A	78.25(5)	N1-Ni1-O1	78.25(5)
N1-Ni1-N3A	90.65(6)	N1-Ni1-O1A	101.75(5)	N3A-Ni1-O1	91.18(6)
N1A-Ni1-N3	90.65(6)	N3A-Ni1-O1A	88.82(6)	N3-Ni1-O1	88.82(6)
N1-Ni1-N3	89.35(6)	N3-Ni1-O1A	91.18(6)	O1A-Ni1-O1	180.0

Symmetry codes: A: 1-x, -y, 1-z for **1**; A: -x, 1-y, 1-z for **2**.

Dash lines indicate that there are hydrogen bonds

Fig.3 Views of the three-dimensional supramolecular architecture of the complex **1**

showing that O1, O1A, N3 and N3A atoms are in the equatorial position. Moreover, the bond angles of O1-Co1-O1A, N3-Co1-N3A, N1-Co1-N1A are also equal to 180°, further indicating that the geometries around each metal center are all octahedral. The lengths of M-O and M-N bonds around the M(II) atom are comparable with those observed in 3,5-pyrazoledicarboxylate based M(II) complexes^[36-37]. As a bidentate ligand, the MPA⁻ anion chelates one M(II) atom with pyrazole N atom and carboxyl O atom to form a five membered ring of M1-O1-C5-C4-N1. The bond lengths of N1-N2, C2-N2, C2-C3, C3-C4, C4-N1 in

pyrazole ring in **1** and **2** are similar to the values seen in mononuclear complex [Zn(mpc)₂(H₂O)₂] (Hmpe=3-methylpyrazole-5-carboxylic acid)^[38]. Besides, there is a kind of intramolecular hydrogen bond C-H···N in **1** and **2**.

As shown in Fig.2, there are also four kinds of intermolecular hydrogen bonds in both of them: (i) hydrogen bonds between the oxygen (donor) from lattice water and oxygen (acceptor) from MPA⁻ ligand: O3-H3X···O1C, O3-H3Y···O2; (ii) hydrogen bonds of an uncoordinated nitrogen (donor) of Im with oxygen (acceptor) from MPA⁻ ligand: N4-H4···O2D; (iii) hydrogen bonds of uncoordinated nitrogen (donor) from MPA⁻ ligand with the oxygen (acceptor) from lattice water: N2-H2···O3B; (iv) hydrogen bonds of carbon (donor) of Im with the oxygen (acceptor) from lattice water: C6-H6···O(3)D. The mononuclear subunits and the lattice water molecules are interlinked via the interaction of three kinds of intermolecular hydrogen bonds N2-H2···O3B, O3-H3X···O1C and O3-H3Y···O2, resulting in the formation of a two-dimensional layer, as shown in Fig.2. These 2D grid-like layers are further packed into a three-dimensional supramolecular architecture through hydrogen bonding

Table 3 Bond lengths and angles of hydrogen bonds in **1** and **2**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
Complex 1				
N2-H2...O3B	0.093	0.194	0.276 5(3)	146
O3-H3X...O1C	0.084	0.194	0.276 9(2)	170
O3-H3Y...O2D	0.082	0.193	0.273 1(2)	165
N4-H4...O2D	0.087	0.196	0.276 2(3)	152
C6-H6...N1	0.093	0.261	0.308 3(3)	112
C6-H6...O3D	0.093	0.257	0.329 6(3)	135
Complex 2				
N2-H2...O3B	0.087	0.191	0.275 1(2)	161
O3-H3A...O2C	0.082	0.195	0.273 0(2)	159
O3-H3B...O1D	0.080	0.199	0.275 7(2)	161
N4-H4...O2E	0.087	0.197	0.277 0(2)	151
C6-H6...N1	0.093	0.260	0.304 5(2)	110
C6-H6...O3F	0.093	0.256	0.330 0(3)	137

Symmetry codes: B: $3/2-x, -1/2+y, 3/2-z$; C: $1/2+x, 1/2-y, 1/2+z$; D: $1/2+x, 1/2-y, -1/2+z$ for **1**; B: $1/2+x, 1/2-y, 1/2+z$; C: $-x, 1-y, 1-z$; D: $-1/2-x, 1/2+y, 1/2-z$; E: $1/2+x, 3/2-y, -1/2+z$; F: $1/2-x, 1/2+y, 1/2-z$ for **2**.

interactions (N4-H4...O2D=0.276 2(3) nm for **1**, N4-H4...O2E=0.277 0 (2) nm for **2** and C6-H6...O3D=0.329 6(3) nm for **1**, C6-H6...O3F=0.330 0(3) nm for **2**) between the adjacent layers, as shown in Fig.3. The length and angles of the hydrogen bonds for **1** and **2** are listed in Table 3.

3.3 Thermogravimetric analyses

So as to examine the thermal stability of these compounds, the thermogravimetric analyses were carried out from ambient temperature up to 800 °C, and the results reveal that both of them possess three main loss stages. For compound **1**, the first weight loss of 7.61% between 25 and 275 °C is attributed to the loss of two lattice water molecules (Calcd. 7.48%). The second degradation stage is in the range 275~389 °C with mass loss of 29.30%, corresponding to the loss of two Im molecules (Calcd. 28.90%), leaving a framework [Co(MPA)₂]. The decomposition of [Co(MPA)₂] starts above 389 °C, and finally degrades to CoO with a loss of 25.33% (Calcd. 25.70%). For compound **2**, the first weight loss of 7.90% which occurred from 61 to 132 °C, corresponds to the release of two lattice water molecules (Calcd. 7.52%). Between 278 °C and 388 °C there is a 53.82% weight loss, corresponding to the loss of a MPA⁻ and two Im molecules (Calcd. 54.46%). Above 388 °C, the remaining part [Ni(MPA)]⁺

gradually degrades to NiO with a loss of 20.57% (Calcd. 21.50%).

3.4 Electrochemical property

Using water as solvent, the concentration of [Co(MPA)₂(Im)₂]·2H₂O (**1**) and [Ni(MPA)₂(Im)₂]·2H₂O (**2**) were 0.5 mmol·L⁻¹. The redox behaviors of the complexes were studied by cyclic voltammetry (CV). Cyclic voltammogram of the complexes are shown in Fig.4 and Fig.5, during scanning from -1.500 to 1.500 V in 100 mV·s⁻¹, the cyclic voltammogram curve of both **1** and **2** only have one pair of oxidation-reduction peak, which corresponds to M(II)/M(III) (**1**: M=Co; **2**: M=Ni) redox process^[39-40]. For **1**, $E_{pa}=-0.61$ V, $E_{pc}=-0.68$ V, $\Delta E=0.07$ V, $E_{1/2}=-0.65$ V; For **2**, $E_{pa}=-0.53$ V, $E_{pc}=-0.54$ V, $\Delta E=0.01$ V, $E_{1/2}=-0.54$ V. The

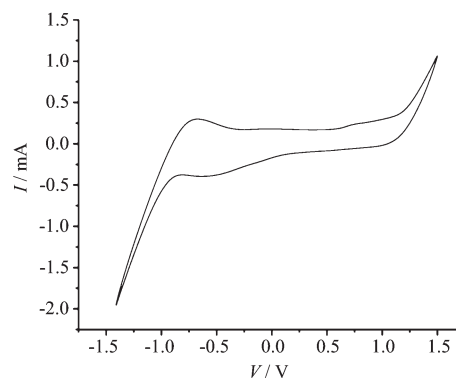


Fig.4 Cyclic voltammogram of complex **1** in aqueous solution

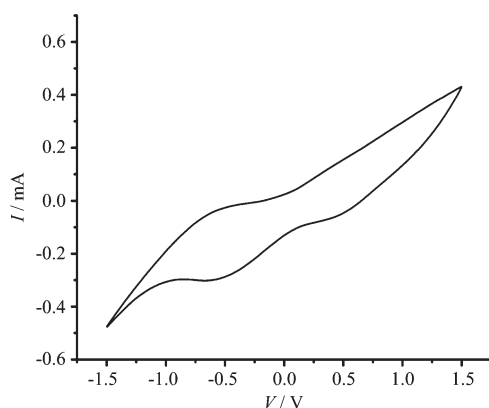


Fig.5 Cyclic voltammogram of complex **2** in aqueous solution

results show that electron transfer of M(II) between M(III) in electrolysis is quasi-reversible process.

4 Conclusions

In summary, we have successfully synthesized two new complexes $[M(\text{MPA})_2(\text{Im})_2] \cdot 2\text{H}_2\text{O}$ (**1**: $M=\text{Co}$; **2**: $M=\text{Ni}$) under slow evaporation condition and characterized by single crystal X-ray diffraction. The monomeric components $[M(\text{MPA})_2(\text{Im})_2] \cdot 2\text{H}_2\text{O}$ are connected by intermolecular hydrogen bonds to form a three-dimensional supramolecular architecture, indicating that the intermolecular hydrogen bond plays an important role in the assembly of these high-dimensional supramolecular architectures. Electrochemical property of the complex shows that electron transfer of M(II) between M(III) ($M=\text{Co}, \text{Ni}$) in electrolysis is quasi-reversible process.

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