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以咪唑为配体的钴和镍的配合物的合成、晶体结构及电化学性质

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摘要:合成了 2 种新颖的配合物[M(ImH)$_6$](tfbdc)(M=Co,Ni;tfbdc=2,3,5,6-四氟对二苯甲酸根;ImH=咪唑),并通过元素分析,红外光谱,热重分析,循环伏安及 X-射线单晶结构分析对其结构及性质进行了表征。2 个配合物[Co(ImH)$_6$](tfbdc) (**1**)和[Ni(ImH)$_6$](tfbdc) (**2**)都属单斜晶系,空间群为 $P2_1/c$,且 Z=2。每 1 个金属离子与来自 6 个咪唑分子的 6 个氮原子配位,形成八面体配位构型。独立组分,[M(ImH)$_6$]$^{2+}$阳离子和四氟对二苯甲酸阴离子之间通过两种氢键(N–H…O 和 C–H…F)连接形成了一种三维的超分子网络结构。

关键词:钴配合物;镍配合物;咪唑;2,3,5,6-四氟对二苯甲酸;晶体结构;电化学性质
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Syntheses, Crystal Structures and Electrochemical Properties of Cobalt and Nickel Complexes Containing Imidazole Ligand

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Abstract: Two novel complexes [M(ImH)$_6$](tfbdc) (M=Co, Ni; ImH=imidazole, tfbdc=2,3,5,6-tetrafluoroterephthalate) were synthesized and characterized by elemental analysis, IR spectra, thermogravimetric analysis, cyclic voltammetry, and X-ray single crystal structure analysis. Both [Co(ImH)$_6$](tfbdc) (**1**) and [Ni(ImH)$_6$](tfbdc) (**2**) all crystallize in the monoclinic system, space group $P2_1/c$, and with Z=2. Metal ions have all octahedral geometry coordinated by six N atoms from six imidazole molecules. The independent components, [M(ImH)$_6$]$^{2+}$ cations and tfbdc anions are connected into a three-dimensional supramolecular network by N–H…O and C–H…F hydrogen bonds. CCDC: 739086, **1**; 739088, **2**.

Key words: cobalt complexes; nickel complex; imidazole; 2,3,5,6-tetrafluoroterephthalate; crystal structure; electrochemical property

0 Introduction

Recently, much attention has been paid to the design and construction of metal-organic frameworks because of their interesting structural motifs[1], and potential applications in gas storage, catalysis, separations, fluorescent and magnetic molecular-based materials[2-6].

Imidazole (ImH) is of considerable interest as a ligand and its presence in many biological systems provides a potential binding site for metal ions[7]. Imidazole itself is usually a unidentate ligand to form

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complexes with metal ions through its nitrogen atom. It has been reported that a large number of imidazole derivatives possess diverse pharmacological effects, including antiinflammatory, antimicrobial, antimalarial and antitumor activities[8].

On the other hand, aromatic multicarboxylic acid, such as 1,4-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid and 2,3,5,6-tetrafluoroterephthalatic acid (H_2tfbdc), are good ligands in the design of metal-organic materials due to its diverse coordination mode. Although H_2tfbdc as well as carboxylate could form various coordination complexes with interesting structures[9-12], the coordination compounds containing H_2tfbdc and ImH have not been reported so far. With the aim of understanding the coordination chemistry of H_2tfbdc and ImH, we recently began to study on the assembly reactions of H_2tfbdc and ImH with metal ions via general solution synthetic methods. Herein, we report the syntheses, crystal structures and electrochemical properties of two three-dimensional supramolecular compounds [$M(ImH)_6$](tfbdc) (M=Co, Ni).

1 Experimental section

1.1 Material

2,3,5,6-tetrafluoroterephthalatic acid (H_2tfbdc), M(Ⅱ) acetate tetrahydrate (M=Co, Ni), imidazole (ImH) and solvents were of reagent grade without further purification before use.

1.2 Physical measurements

The elemental analysis(C, H, 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 complex was carried out with a Bruker Smart Apex CCD diffractometer at 296(2) K. Thermogravimetric analysis (TGA) experiments were carried out on a Dupont thermal analyzer from room temperature to 800 ℃ under N_2 atmosphere at a heating rate of 10 ℃·min^{-1}. 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 mol·L^{-1} NaCl. The half wave potentials $E_{1/2}$ were obtained from $(E_{pa}+E_{pc})/2$.

1.3 Preparation of [Co(ImH)$_6$](tfbdc) (1)

$Co(OAc)_2\cdot 4H_2O$ (0.024 9 g, 0.1 mmol), H_2tfbdc (0.047 6 g, 0.2 mmol) and ImH (0.068 1 g, 1 mmol) were added into a mixed solvent of 4 mL anhydrous methanol and 2 mL water and stirred for several minutes to afford an orange solution. The resulting solution was allowed to stand at ambient temperature for several days, yielding orange crystals. [0.048 5 g, 69% yield, (based on Co)]. Anal. Calcd. for $C_{26}H_{24}CoF_4N_{12}O_4$ (%): C 44.39 (44.50), H 3.44 (3.31), N 23.90 (23.95). I.R. data (cm^{-1}, KBr pellet): 3 203(s), 3 172(s), 3 071(m), 2 953(m), 2 865 (m), 1 627(s), 1 527(m), 1 465(m), 1 371(s), 1 329(m), 1 257(m), 1 248(m), 1 169(m), 1 130(w), 1 093(m), 1 069 (s), 985(s), 943(m), 880(m), 782(m), 734(s), 661(s), 617 (s), 475(m), 408(w).

1.4 Preparation of [Ni(ImH)$_6$](tfbdc) (2)

The same synthetic procedure as that for **1** was used except $Co(OAc)_2\cdot 4H_2O$ was replaced by $Ni(OAc)_2\cdot 4H_2O$ (0.024 9 g, 0.1 mmol). The blue single crystals of **2** suitable for X-ray analysis were obtained [0.049 9 g, 71% yield, (based on Ni)]. Anal. Calcd. For $C_{26}H_{24}NiF_4N_{12}O_4$(%): C 44.40 (44.47), H 3.44 (3.36), N 23.91 (23.93). I.R. data (cm^{-1}, KBr pellet): 3 138(s), 2 947(m), 2 861(m), 2 622(w), 2 367(w), 1 625(s), 1 538(m), 1 468 (s), 1 360(s), 1 326(m), 1 255(m), 1 169(m), 1 145(w), 1 097(m), 1 068(s), 984(s), 940(m), 830(m), 757(s), 729 (s), 664(s), 616(s), 468(m).

1.5 X-ray crystallography

Single-crystal X-ray diffraction measurement of **1** and **2** were carried out with a Bruker Smart Apex CCD diffractometer at 296(2) K. Intensities of reflections were measured using graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) with the φ-ω scans mode in the range of $2.02°\leqslant\theta\leqslant 27.55°$ (for **1**) and $2.02°\leqslant\theta\leqslant 27.63°$ (for **2**). The structures were solved by direct methods using SHELXS97[13] 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. Crystallographic data parameters for structural analyses are summarized in Table 1, the selected bond lengths (nm) and bond angles (°) are given in Table 2, and the hydrogen bond distances and angles in the complex are presented in Table 3, respectively.

CCDC: 739086, **1**; 739088, **2**.

Table 1　Crystallographic data for complexes 1 and 2

Compound	**1**	**2**
Empirical formula	$C_{26}H_{24}CoF_4N_{12}O_4$	$C_{26}H_{24}NiF_4N_{12}O_4$
Formula weight	703.5	703.28
T / K	296(2)	296(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / nm	0.744 1(3)	0.746 7(5)
b / nm	1.466 2(5)	1.462 1(10)
c / nm	1.411 5(5)	1.407 2(10)
β / (°)	99.525(4)	99.621(8)
V / nm^3	1.518 7(9)	1.514 7(18)
Z	2	2
D_c / (g·cm^{-3})	1.538	1.542
Mu (Mo $K\alpha$) / mm^{-1}	0.645	0.72
F(000)	718	720
Crystal size / mm	0.30×0.20×0.20	0.20×0.20×0.15
θ range for data collection / (°)	2.02 to 27.55	2.02 to 27.63
Index ranges	−9/9,−19/19,−18/18	−9/9, −18/18, −18/18
Reflections collected / unique (R_{int})	13 062 / 3 503 (0.028 0)	12 161 / 3 486 (0.053 7)
Completeness to 2θ / %	99.9	98.8
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3 503 / 0 / 214	3 486 / 0 / 214
Goodness- of-fit on F^2	1.038	1.117
R_1, wR_2 ($I>2\sigma(I)$)	0.031 4, 0.078 1	0.048 5, 0.120 9
R_1, wR_2 (all data)	0.038 3, 0.082 0	0.062 4, 0.128 8
Largest diff. peak and hole / (e·nm^{-3})	246 and −288	674 and −1 037

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

Compound **1**					
Co1-N1	0.220 88(14)	Co1-N3#1	0.214 55(13)	O(1)-C(13)	0.124 91(18)
Co1-N1#1	0.220 88(14)	Co1-N5	0.217 85(14)	O(2)-C(13)	0.124 1(2)
Co1-N3	0.214 55(13)	Co1-N5#1	0.217 85(14)		
N3#1-Co1-N3	180.00(5)	N5-Co1-N5#1	180.0	N3#1-Co1-N1#1	89.95(5)
N3#1-Co1-N5	89.60(6)	N3#1-Co1-N1	90.05(5)	N3-Co1-N1#1	90.05(5)
N3-Co1-N5	90.40(6)	N3-Co1-N1	89.95(5)	N5-Co1-N1#1	91.54(5)
N3#1-Co1-N5#1	90.40(6)	N5-Co1-N1	88.46(5)	N5#1-Co1-N1#1	88.46(5)
N3-Co1-N5#1	89.60(6)	N5#1-Co1-N1	91.54(5)	N1-Co1-N1#1	180.0

Continued Table 2

Compound **2**					
Ni1-N1	0.217 0(2)	Ni1-N3#1	0.214 4(2)	O(1)-C(13)	0.125 2(3)
Ni1-N1#1	0.217 0(2)	Ni(1)-N(5)	0.211 4(2)	O(2)-C(13)	0.125 0(3)
Ni1-N3	0.214 4(2)	Ni(1)-N(5)#1	0.211 4(2)		
N5-Ni1-N5#1	180.0	N3-Ni1-N3#1	180.0	N5-Ni1-N1#1	89.84(9)
N5-Ni1-N3	90.16(10)	N5-Ni1-N1	90.16(9)	N5#1-Ni1-N1#1	90.16(9)
N5#1-Ni1-N3	89.84(10)	N5#1-Ni1-N1	89.84(9)	N3-Ni1-N1#1	91.17(9)
N5-Ni1-N3#1	89.84(9)	N3-Ni1-N1	88.83(9)	N3#1-Ni1-N1#1	88.83(9)
N5#1-Ni1-N3#1	90.16(10)	N3#1-Ni1-N1	91.17(9)	N1-Ni1-N1#1	180.0

Symmetry codes: **1**: #1: $-x+1, -y, -z+2$; #2: $-x+1, -y, -z+1$; **2**: #1: $-x+2, -y, -z+1$; #2: $-x, -y+1, -z+1$.

Table 3 Hydrogen bond distances and angles for complexes 1 and 2

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D-A) / nm	∠D–H···A / (°)
Compound **1**				
N6–H6B···O1	0.086	0.197	0.280 0(2)	160.5
N2–H2B···O1#3	0.086	0.198	0.281 76(19)	165.2
N4–H4B···O2#4	0.086	0.191	0.274 3(2)	162.9
C6–H6A···F1#5	0.093	0.234	0.297 3(2)	124.7
Compound **2**				
N2–H2B···O1	0.086	0.199	0.282 2(3)	164.0
N4–H4B···O1#3	0.086	0.199	0.280 9(3)	159.8
N6–H6B···O2#4	0.086	0.192	0.275 4(3)	161.6
C9–H9A···F1#5	0.093	0.234	0.296 2(4)	124.0

Symmetry codes: **1**: #3: $x+1, -y+1/2, z+1/2$; #4: $x, y, z+1$; #5: $x, -y+1/2, z+1/2$; **2**: #3: $x+1, -y+1/2, z+1/2$; #4: $x+1, -y+1/2, z-1/2$; #5: $x+1, y, z$.

2 Results and discussion

2.1 Infrared spectrum

The complexes **1** and **2** all have quite similar infrared spectra and reflects the binding patterns of ImH, and 2,3,5,6-tetrafluoroterephthalate moieties. Carboxylic group of the organic ligand in the compound is deprotonated, in agreement with the IR spectrum results, where no absorption peak around 1 730~1 700 cm^{-1} for a protonated carboxylic group is observed. The strong absorption band in the 3 600~3 000 cm^{-1} regions corresponds to ν(C-H) of the coordination ImH molecules[7]. For $[Co(ImH)_6](tfbdc)$ (**1**), the strong peaks at 1 627, 1 465 and 1 371 cm^{-1} are the ν_{as}(OCO), and ν_s(OCO) stretching mode of the coordinated tfbdc, while strong absorption at *ca.* 985 cm^{-1} is the δ(OCO) bent vibration of tfbdc[9]. The peaks at 1 527 cm^{-1} is characteristic ν_{as}(C=N) of the coordinated ImH. For $[Ni(ImH)_6](tfbdc)$ (**2**), the strong peaks at 1 625, 1 468 and 1 360 cm^{-1} are the ν_{as}(OCO), and ν_s(OCO) stretching mode of the coordinated tfbdc, while strong absorption at *ca.* 984 cm^{-1} is the δ(OCO) bent vibration of tfbdc. The peaks at 1 538 cm^{-1} is characteristic ν_{as}(C=N) of the coordinated ImH.

2.2 Description of crystal structures

Fig.1 shows a perspective view of the title compounds with atomic numbering scheme. The asymmetric unit of $[M(ImH)_6](tfbdc)$ (M=Co, Ni) consists of one-half of a monomeric $[M(ImH)_6]^{2+}$ (M=Co, Ni) cation and a tfbdc anion, linked by electrostatic forces and hydrogen bonds, The other halves are generated by crystallographic inversion centres, while the metal ion lies on a crystallographic inversion centre. The coordination mode of the M^{II} atom can be described as an MN_6 chromophore, with octahedral geometry. Six imidazole molecules are coordinated through their

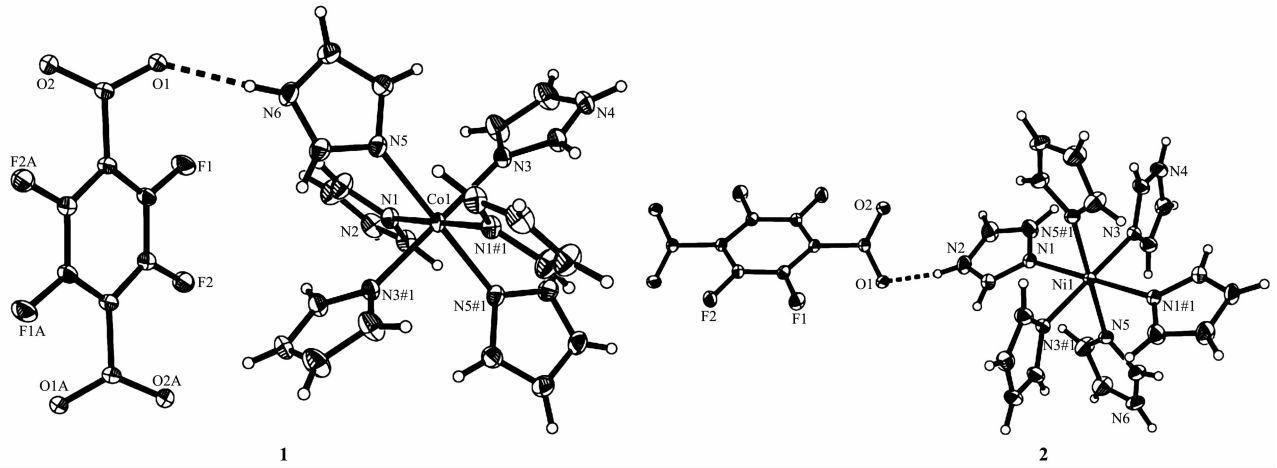


Fig.1　Molecular structure of the title compounds, dashed lines indicate intramolecular hydrogen bonds

tertiary N atoms to each M^{II} ion and one tfbdc group is outside the coordination sphere, balancing the charge.

For $[Co(ImH)_6](tfbdc)$, the Co1-N5, Co1-N1 and Co1-N3 bond distances are 0.217 85 (14), 0.220 88(14) and 0.214 55(13) nm, respectively (Table 2). All these bond distances are longer than the Co-N distances observed in catena-(tris(2,2′-Bi-imidazole-*N*,*N*′)-cobalt (Ⅱ)(μ_2-2,2′-bi-imidazolato-*N*,*N*′,*N*″)-(μ_2-benzene-1,3,5-tricarboxylato-*O*,*O*′)-cobalt(Ⅱ) dihydrate)[14]. All the imidazole rings are planar. In the tfbdc moiety, the $-COO^-$ group is slightly twisted away from the aromatic ring, with the O1-C13-C10-C11 and O2-C13-C10-C12 torsion angles of 41.3(2)° and 39.4(2)°. For $[Ni(ImH)_6](tfbdc)$, the Ni1-N5, Ni1-N1 and Ni1-N3 bond distances are 0.211 4(2), 0.217 0(2) and 0.214 4(2) nm, respectively (Table 2). All these bond distances are longer than the Ni-N distances observed in Tris (2,2′-biimidazole) nickel(Ⅱ) phthalate correspondingly[15]. All the imidazole rings are planar. In the tfbdc moiety, the $-COO^-$ group is slightly twisted away from the aromatic ring, with the O1-C13-C10-C11 and O2-C13-C10-C12 torsion angles of 41.0(4)° and 39.4(4)°. In each crystal structure, the independent components, $[M(ImH)_6]^{2+}$ cations and tfbdc anions are connected by two kinds of hydrogen bonds (N–H⋯O and C–H⋯F) to form a three-dimensional supramolecular network, as shown in Fig.2.

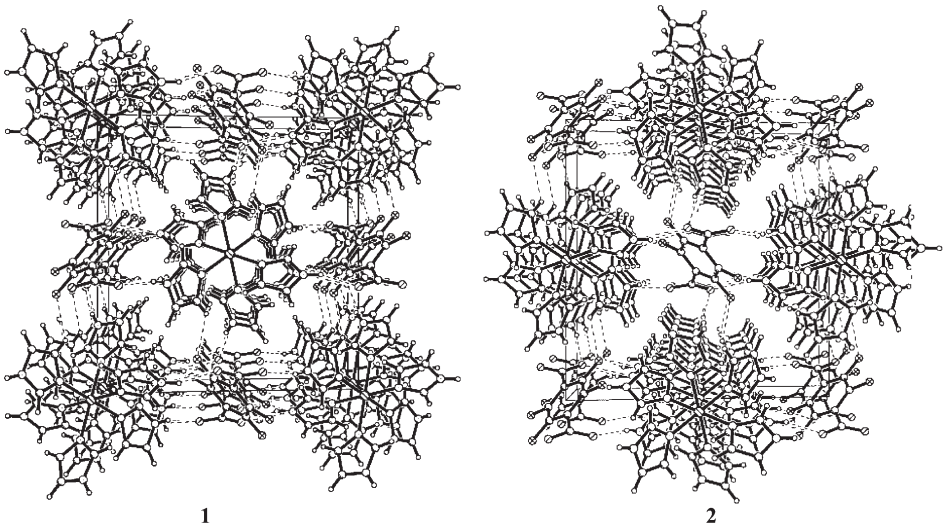


Fig.2　Views of the three-dimensional hydrogen-bonded networks of the title compounds, dashed lines indicate hydrogen bonds

2.3　Thermal stability

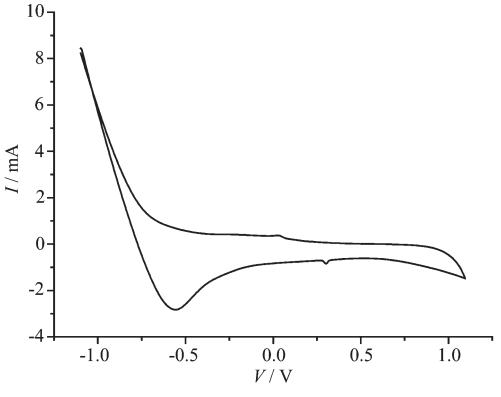
Thermal stability of coordination compound $[Co(ImH)_6](tfbdc)$ (**1**) has been investigated by TG technique, The TG analysis shows that weight loss of $[Co(ImH)_6](tfbdc)$ begins at 120 ℃, and six Him molecules are lost from 120 ℃ to 196 ℃ (calculated,

58.06%; found, 58.60%). The second weight loss of 30.65% at 196~800 ℃ corresponds to the loss of the tfbdc molecule (calculated 31.28%). The pyrolysis product is CoO (calculated, 10.65%; found, 10.75%).

Thermal behavior of coordination compound $[Ni(ImH)_6](tfbdc)$ (**2**) is quite similar to **1**. The TG analysis shows that weight loss of $[Ni(ImH)_6](tfbdc)$ begins at 135 ℃, and six ImH molecules are lost from 135 to 212 ℃ (calculated, 58.08%; found, 59.60%). The second weight loss of 30.46% at 212~800 ℃ corresponds to the loss of the tfbdc molecule (calculated 31.30%). The pyrolysis product is NiO (calculated, 10.63%; found, 9.94%).

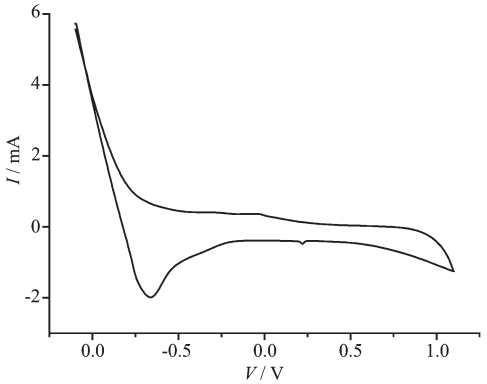
2.4 Electrochemical property

Using water as solvent, the concentration of $[Co(ImH)_6](tfbdc)$ and $[Ni(ImH)_6](tfbdc)$ were 0.550 mmol·L^{-1} and 0.540 mmol·L^{-1}, respectively. The redox behavior of the $[M(ImH)_6](tfbdc)$ (M=Co, Ni) complexes were studied by cyclic voltammetry (CV). Cyclic voltammograms of compounds $[Co(ImH)_6](tfbdc)$ and $[Ni(ImH)_6](tfbdc)$ are shown in Fig.3 and Fig.4 respectively, which are quite similar, during scanning from −1.1 to 1.1 V in 100 mV·s^{-1}, the cyclic voltammogram curve only has an oxidation-reduction peak, which corresponds to M(Ⅱ)/M(Ⅲ) redox process[16-18], For $[Co(ImH)_6](tfbdc)$, E_{pa}=0.30 V, E_{pc}=0.028 V, ΔE=0.272 V. The results show that electron transfer of Co(Ⅱ) between Co(Ⅲ) in electrolysis is quasi-reversible process. For $[Ni(ImH)_6](tfbdc)$, E_{pa}=0.22 V, E_{pc}=−0.1 V, ΔE=0.23 V, which show that electron transfer of Ni(Ⅱ) between Ni(Ⅲ) in electrolysis is quasi-reversible process, too.



Concentration: 0.550 mmol·L^{-1}, scan rate 100 mV·s^{-1}

Fig.3 Cyclic voltammogram of $[Co(ImH)_6](tfbdc)$ (**1**) in aqueous solution



Concentration: 0.540 mmol·L^{-1}, scan rate 100 mV·s^{-1}

Fig.4 Cyclic voltammogram of $[Ni(ImH)_6](tfbdc)$ (**2**) in aqueous solution

3 Conclusion

We have synthesized two novel complexes $[Mn(ImH)_6](tfbdc)$ (M=Co, Ni) via general solution synthetic methods. They consist of two independent units: the monomeric cation $[M(ImH)_6]^{2+}$ and the tfbdc anion. The $[M(ImH)_6]^{2+}$ cations and tfbdc anions are connected by N–H···O and C–H···F hydrogen bonds to form a three-dimensional supramolecular architecture. Electrochemical property of the complex shows that electron transfer of between M(Ⅱ) and M(Ⅲ) (M=Co, Ni) in electrolysis is quasi-reversible process.

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