

2-噻吩咪唑[4,5-*f*][1,10]菲啰啉及其衍生物的 顺式镉(II)、锰(II)和镍(II)配合物的结构和波谱研究

王银歌¹ 刘前前² 翟立新¹ 钱惠芬^{*,1,2} 黄 伟^{*,2}

(¹南京工业大学理学院, 南京 210009)

(²南京大学化学化工学院, 南京微结构国家实验室, 配位化学国家重点实验室, 南京 210093)

摘要: 本文报道了 3 个基于 2-噻吩咪唑[4,5-*f*][1,10]菲啰啉(TIP)和 2-(5-溴-2-噻吩)咪唑[4,5-*f*][1,10]菲啰啉(5-Br-TIP)的镉(II)配合物 **1** [*cis*-Cd(TIP)₂(NO₃)₂]、锰(II)配合物 **2** [*cis*-Mn(5-Br-TIP)₂Cl₂]和镍(II)配合物 **3** [*cis*-Ni(TIP)₂Cl(CH₃OH)]Cl·CH₃OH 的合成、波谱和晶体结构表征。它们均为顺式 1:2 单核配合物, 其中 **1** 为 8 配位, **2** 和 **3** 为 6 配位, TIP 和 5-Br-TIP 配体在不同配合物中噻吩和邻菲啰啉并咪唑环之间的二面角有所不同, 但都不大, 在 3.9(1)°~9.2(1)°范围。

关键词: 镉(II)配合物; 锰(II)配合物; 镍(II)配合物; 2-噻吩咪唑[4,5-*f*][1,10]菲啰啉; 2-(5-溴-2-噻吩)咪唑[4,5-*f*][1,10]菲啰啉; 晶体结构

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Structural and Spectral Studies of *Cis* Cadmium(II), Manganese(II) and Nickel(II) Complexes Having 2-Thiophenimidazo[4,5-*f*][1,10]phenanthroline and 2-(5-Bromothiophen)imidazo[4,5-*f*][1,10]phenanthroline Ligands

WANG Yin-Ge¹ LIU Qian-Qian² ZHAI Li-Xin¹ QIAN Hui-Fen^{*,1,2} HUANG Wei^{*,2}

(¹College of Sciences, Nanjing University of Technology, Nanjing 210009, China)

(²State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures,
School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China)

Abstract: Three mononuclear cadmium(II), manganese(II) and nickel(II) complexes having 2-thiophenimidazo[4,5-*f*][1,10]phenanthroline (TIP) and 2-(5-bromothiophen)imidazo[4,5-*f*][1,10]phenanthroline (5-Br-TIP) ligands formulated as [*cis*-Cd(NO₃)(TIP)₂] (**1**), [*cis*-MnCl₂(5-Br-TIP)₂] (**2**) and [*cis*-NiCl₂(TIP)₂] (**3**), have been synthesized and structurally compared. They are characterized by elemental analysis, FT-IR, UV-Vis spectra, luminescence spectra and X-ray single-crystal structural analysis. All of them are 1:2 mononuclear complexes with the same *cis* configuration, among which complex **1** is eight-coordinated and the others are six-coordinated. Ligands TIP and 5-Br-TIP in complex **1**~**3** are essentially planar with the dihedral angles between imidazole and thiophene rings in the range of 3.9(1)°~9.2(1)°. CCDC: 922633, **1**; 922634, **2**; 922635, **3**.

Key words: cadmium(II) complex; manganese(II) complex; nickel(II) complex; 2-thiophenimidazo[4,5-*f*][1,10]phenanthroline; 2-(5-bromothiophen)imidazo[4,5-*f*][1,10]phenanthroline; crystal structure

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*通讯联系人。E-mail: qhf@njut.edu.cn, whuang@nju.edu.cn

0 Introduction

As we know, π -conjugated organic compounds have attracted much attention and emerged as a class of functional materials with very promising properties owing to their wide-ranging applications on DNA detection^[1-2], chemical sensors^[3-4], organic semiconducting laser^[5], dye-sensitized solar cells^[6-8], organic field-effect transistors^[9-10]. Among them, coordination chemistry of 1,10-phenanthroline (phen) derivatives with extended π -system has become a major topic of research. These metal complexes have shown potential applications on photonics, optoelectronics, solar cells and molecular probes and so on^[11-16]. In particular, imidazo[4,5-*f*][1,10]phenanthroline derivatives grafted by different heteroaromatic rings have been an important race because of their symmetrical and asymmetrical structures as well as pH dependency and luminescence sensitivity. Moreover, the imidazole-containing phenanthroline ligands are constituted by parts of both electron acceptors and electron donors, which may tune the ground and excited state properties of the complexes^[17-23].

Our previous research in this area has been mainly focused on the linear 3,8- and planar 5,6-extended 1,10-phenanthroline-based heterocyclic aromatic fluorescent compounds showing semiconducting, photoresponsive and chemosensing properties^[24]. In this paper, three mononuclear cadmium (II), manganese (II) and nickel(II) coordination complexes of 2-thiophenimidazo[4,5-*f*][1,10]phenanthroline (TIP) and 2-(5-bromothiophen)imidazo[4,5-*f*][1,10]phenanthroline (5-Br-TIP) ligands, bearing the same 1:2 metal/ligand molar ratio and *cis* configuration, are prepared and characterized. They are formulated as [*cis*-Cd(NO₃)(TIP)₂] (1), [*cis*-MnCl₂(5-Br-TIP)₂] (2) and [*cis*-NiCl₂(TIP)₂] (3), and their single-crystal structures, UV-Vis and luminescence spectra have been described in detail.

1 Experimental

1.1 Materials and instruments

All reagents and solvents were of analytical grade and used without any further purification. Ligands

TIP^[25] and 5-Br-TIP^[26] were prepared via previously reported approaches.

Elemental analyses (EA) for carbon, hydrogen, and nitrogen were performed on a Perkin-Elmer 1400C analyzer. Fourier transform infrared (FT-IR) spectra (4 000~400 cm⁻¹) were recorded using a Nicolet FT-IR 170X spectrophotometer on KBr disks. UV-vis spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm. Luminescence spectra were recorded on an F-4600 fluorescence spectrophotometer at room temperature (25 °C) using the same solutions as those for the UV-Vis determination.

1.2 Syntheses of the 1:2 mononuclear metal complexes

Preparation of the cadmium(II) complex [*cis*-Cd(TIP)₂(NO₃)₂] (1). A mixture of TIP (24.1 mg, 0.08 mmol), Cd(NO₃)₂·4H₂O (12.34 mg, 0.04 mmol), water (0.6 cm³) and methanol (12.0 cm³) was frozen and sealed under a vacuum in a thick-walled Pyrex tube, then placed inside an oven at 120 °C for 40 h. The yellow block crystals were obtained in a yield of 20.2 mg (60%) on the basis of TIP. Main FT-IR absorptions (KBr pellets, ν / cm⁻¹): 3 427(b), 3 220(m), 3 112(w), 1 612(m), 1 573(s), 1 514(w), 1 485(m), 1 460(m), 1 394 (s), 1 359 (m), 1 299 (s), 1 236 (m), 1 130(w), 1 178(m), 1 033(w), 925(w), 858(w), 813(m), 734(m), 713(m), 663(w). Fluorescence in CH₃OH at room temperature: $\lambda_{\text{max, em}}$ =508 nm, $\lambda_{\text{max, ex}}$ =283 nm. Elemental analysis: Calcd.(%) for C₃₄H₂₀CdN₁₀O₆S₂: C, 48.55; H, 2.40; N, 16.65; Found (%): C, 48.44; H, 2.54; N, 16.50. UV-Vis (CH₃OH): λ_{max} =292 and 328 nm. Negative ESI-MS peak (*m/z*): 776, [Cd(NO₃)₂(TIP)(C₂H₆O)₃(CH₄O)₂(H₂O)₂-H]⁻.

Preparation of the manganese(II) complex [*cis*-Mn(5-Br-TIP)₂Cl₂] (2). A mixture of 5-Br-TIP (30.5 mg, 0.08 mmol), MnCl₂·4H₂O (7.8 mg, 0.04 mmol), water (0.6 cm³) and methanol (12.0 cm³) was frozen and sealed under a vacuum in a thick-walled Pyrex tube, then placed inside an oven at 120 °C for 40 h. The yellow block crystals were obtained in a yield of 21.3 mg (60%) on the basis of TIP. Main FT-IR absorptions (KBr pellets, ν / cm⁻¹): 3 409(b), 3 074(m), 1 610(m),

1 571(m), 1 527(w), 1 487(s), 1 456(m), 1 438(m), 1 402(m), 1 355(m), 1 184(w), 1 130(w), 1 085(m), 1 045(w), 920(w), 810(m), 734(s), 700(w), 628(m). Fluorescence in CH₃OH at room temperature: $\lambda_{\text{max, em}}$ = 447 nm, $\lambda_{\text{max, ex}}$ = 277 nm. Elemental analysis: Calcd.(%) for C₃₄H₁₈Br₂Cl₂MnN₈S₂: C, 45.97; H, 2.04; N, 12.61. Found (%): C, 45.83; H, 2.21; N, 16.50. UV-Vis (CH₃OH): λ_{max} = 290 and 340 nm. Positive ESI-MS peak (*m/z*): 887, [Mn(5-Br-TIP)₂Cl₂-H]⁺.

Preparation of the nickel(II) complex [*cis*-Ni(TIP)₂Cl(CH₃OH)]Cl·CH₃OH (**3**). A mixture of TIP (24.1 mg, 0.08 mmol), NiCl₂·6H₂O (9.4 mg, 0.04 mmol), water (0.6 cm³) and methanol (12.0 cm³) was frozen and sealed under a vacuum in a thick-walled Pyrex tube, then placed inside an oven at 120 °C for 40 h. The green block crystals were obtained in a yield of 19.1 mg (60%) on the basis of TIP. Main FT-IR absorptions (KBr pellets, ν / cm⁻¹): 3 377(b), 1 608(m), 1 569(m), 1 514(w), 1 483(m), 1 458(w), 1 444(m), 1 404(m), 1 359(m), 1 319(w), 1 238(w), 1 132(w), 1 082(m), 929(w), 813(m), 733(s), 715(w). Elemental analysis: Calcd.(%) for C₃₆H₂₆Cl₂N₈NiO₂S₂: C, 54.29; H, 3.29; N, 14.07; Found (%): C, 50.02; H, 3.34; N, 13.98. UV-Vis (CH₃OH): λ_{max} = 294 and 328 nm. Negative ESI-MS peak (*m/z*): 719, [NiCl₂(TIP)(C₂H₆O)₃(CH₄O)₃

(H₂O)₃-H]⁻.

1.3 X-ray data collection and solution

Single-crystal samples of **1~3** were glue-covered and mounted on glass fibers and then used for data collection at 291(2) K. The diffraction data were collected on a Bruker SMART 1K CCD diffractometer using graphite mono-chromated Mo *K*α radiation (λ = 0.071 073 nm). The crystal systems were determined by the Laue symmetry and the space groups were assigned on the basis of systematic absences using XPREP. Absorption corrections were performed to all data and the structures were solved by direct methods and refined by full-matrix least-squares method on F_{obs}^2 by using the SHELXTL-PC software package^[27-29]. All non-H atoms were anisotropically refined and all hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The summary of the crystal data, experimental details and refinement results for complex **1~3** is listed in Table 1, while selected bond distances and bond angles related to the central Cd(II), Mn(II) and Ni(II) ions are given in Table 2. Hydrogen bonding interactions in complex **1~3** are shown in Table 3.

CCDC: 922633, **1**; 922634, **2**; 922635, **3**.

Table 1 Crystal data and structure refinement parameters for complex **1~3**

Complex	1	2	3
Empirical formula	CdC ₃₄ H ₂₀ N ₁₀ O ₆ S ₂	MnC ₃₄ H ₁₈ Br ₂ Cl ₂ N ₈ S ₂	NiC ₃₆ H ₂₈ Cl ₂ N ₈ O ₂ S ₂
Formula weight	841.15	888.34	798.39
Crystal size / mm	0.10×0.11×0.12	0.10×0.10×0.11	0.10×0.11×0.11
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / nm	1.608 7(2)	1.084 8(3)	1.299 4(2)
<i>b</i> / nm	1.106 2(2)	1.289 3(3)	1.516 2(3)
<i>c</i> / nm	1.852 0(2)	1.417 4(4)	1.739 7(3)
α / (°)		70.612(4)	
β / (°)	99.047(2)	71.484(5)	99.282(3)
γ / (°)		69.569(5)	
<i>V</i> / nm ³	3.254 8(7)	1.706 1(8)	3.382 6(10)
<i>Z</i>	4	2	4
<i>D_c</i> / (g·cm ⁻³)	1.717	1.729	1.564
<i>F</i> (000)	1 688	878	1640
μ (Mo <i>K</i> α) / mm ⁻¹	0.865	3.048	0.904
Max. / min. transmission	0.918 5 / 0.903 3	0.750 3 / 0.730 4	0.915 0 / 0.907 1

Continued Table 1

Limiting indices	$-17 \leq h \leq 19,$ $-13 \leq k \leq 12,$ $-21 \leq l \leq 12$	$-12 \leq h \leq 12,$ $-15 \leq k \leq 15,$ $-16 \leq l \leq 16$	$-15 \leq h \leq 15,$ $-17 \leq k \leq 12,$ $-20 \leq l \leq 19$
Parameters	228	442	449
Reflections collected	8 055	12 188	16 923
Independent reflections (R_{int})	2 852 (0.048)	5 971 (0.101)	5 933 (0.068)
Observed reflections ($I > 2\sigma(I)$)	2 352	2 590	2 902
R_1, wR_2 ($I > 2\sigma(I)$)	0.045 6, 0.110 8	0.058 6, 0.073 9	0.054 4, 0.126 3
R_1, wR_2 (all data)	0.056 2, 0.116 5	0.176 7, 0.091 9	0.117 2, 0.141 9
Goodness of fit on F^2	1.069	0.817	0.869
$(\Delta\rho)_{max}, (\Delta\rho)_{min}$ / (e \cdot nm $^{-3}$)	1 197, -1 631	455, -519	1 223, -664

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

Table 2 Selected bond distances (nm) and angles ($^\circ$) for complex 1-3

1					
Cd1-N2	0.233 9(3)	Cd1-N1	0.247 5(3)	Cd1-O2	0.252 0(3)
Cd1-O1	0.245 0(3)				
N2-Cd1-N2	100.2(2)	O1-Cd1-N1	80.7(1)	O1-Cd1-O2 ⁱ	78.5(1)
N2-Cd1-O1	148.2(1)	O1-Cd1-N1 ⁱ	125.2(1)	N1-Cd1-O2	130.6(1)
N2-Cd1-O1 ⁱ	85.9(1)	N1-Cd1-N1	140.0(2)	N1-Cd1-O2 ⁱ	80.0(1)
O1-Cd1-O1	105.4(2)	N2-Cd1-O2	160.1(1)	O2-Cd1-O2	92.0(2)
N2-Cd1-N1	68.8(1)	N2-Cd1-O2 ⁱ	87.2(1)		
N2-Cd1-N1 ⁱ	85.6(1)	O1-Cd1-O2	50.1(1)		
2					
Mn1-N6	0.226 4(5)	Mn1-N2	0.229 4(6)	Mn1-Cl2	0.245 0(2)
Mn1-N1	0.228 1(5)	Mn1-N5	0.233 0(5)	Mn1-Cl1	0.246 8(2)
N6-Mn1-N1	155.4(2)	N2-Mn1-N5	82.1(2)	N6-Mn1-Cl1	96.0(2)
N6-Mn1-N2	92.0(2)	N6-Mn1-Cl2	98.6(2)	N1-Mn1-Cl1	101.5(1)
N1-Mn1-N2	71.3(2)	N1-Mn1-Cl2	95.7(2)	N2-Mn1-Cl1	89.2(1)
N6-Mn1-N5	71.7(2)	N2-Mn1-Cl2	166.1(2)	N5-Mn1-Cl1	164.5(1)
N1-Mn1-N5	87.8(2)	N5-Mn1-Cl2	92.7(1)	Cl2-Mn1-Cl1	98.5(8)
3					
Ni1-N6	0.206 1(4)	Ni1-N2	0.208 4(4)	Ni1-O1	0.212 3(4)
Ni1-N1	0.207 8(4)	Ni1-N5	0.209 0(4)	Ni1-Cl1	0.243 0(2)
N6-Ni1-N1	171.2(2)	N2-Ni1-N5	88.4(2)	N6-Ni1-Cl1	91.2(1)
N6-Ni1-N2	96.0(2)	N6-Ni1-O1	93.9(2)	N1-Ni1-Cl1	93.9(1)
N1-Ni1-N2	79.5(2)	N1-Ni1-O1	93.4(2)	N2-Ni1-Cl1	172.0(1)
N6-Ni1-N5	80.0(2)	N2-Ni1-O1	87.1(2)	N5-Ni1-Cl1	96.5(2)
N1-Ni1-N5	92.3(2)	N5-Ni1-O1	172.0(2)	O1-Ni1-Cl1	87.7(1)

Symmetry code: 1: $1-x, -y, 2-z$.

Table 3 Hydrogen bonding interactions in complex 1~3

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
1				
N4-H4...O2 ⁱ	0.086	0.208	0.281 6(5)	143.0
C1-H1...O1	0.093	0.253	0.317 2(5)	127.0
C9-H9...O1 ⁱⁱ	0.093	0.241	0.327 9(6)	156.0
2				
N4-H4...Cl1 ⁱⁱⁱ	0.086	0.239	0.322 1(7)	163.0
N8-H8A...Cl2 ^{iv}	0.086	0.230	0.310 3(6)	155.0
C18-H18...Br1 ^v	0.093	0.287	0.358 8(8)	135.0
C20-H20...Cl2 ^{iv}	0.093	0.282	0.367 5(7)	153.0
3				
O1-H1A...Cl2 ^{vi}	0.097	0.234	0.306 9(5)	132.0
C1-H1...Cl1	0.093	0.275	0.335 7(7)	124.0
C26-H26...N3 ^{vii}	0.093	0.261	0.339 7(7)	142.0
C32-H32...Cl2 ^{viii}	0.093	0.287	0.364 0(6)	151.0

Symmetry codes: ⁱ *x*, 1-*y*, 1/2+*z*; ⁱⁱ 1/2+*x*, -1/2+*y*, *z*; ⁱⁱⁱ 2-*x*, -*y*, 2-*z*; ^{iv} 2-*x*, 1-*y*, 1-*z*; ^v 1-*x*, -*y*, 2-*z*; ^{vi} 1-*x*, 1-*y*, 1-*z*; ^{vii} 1+*x*, *y*, *z*; ^{viii} 1+*x*, 1/2-*y*, -1/2+*z*.

2 Results and discussion

2.1 Synthesis and spectral characterizations

In the synthesis of metal complex **1~3** of TIP and 5-Br-TIP, different metal/ligand molar ratios have been employed from 1:1 to 1:3. However, all of the products are proved to be 1:2 complexes. It is suggested that the nature of metal center such as charge, radius, coordination geometry and electronic structure as well as the presence of different counterions may play important roles in altering the molar ratios of products.

UV-Vis absorption spectra of compounds **1~3** have been recorded in the wavelength range of 200~600 nm in CH₃OH (1.0×10⁻⁵ mol·L⁻¹) at room temperature. As shown in Fig.1, the absorption band profiles for

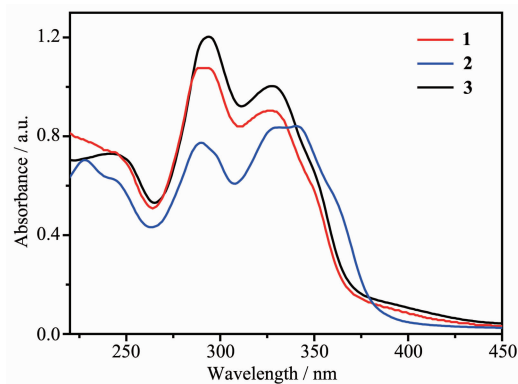


Fig.1 UV-Vis absorption spectra for **1~3** in CH₃OH at room temperature

them at high-energy band are similar, where two sets of UV-Vis absorption peaks at 290~293 and 327~341 nm are observed in **1~3**, respectively, corresponding to the π - π^* transition of the extended heterocyclic aromatic ligands TIP and 5-Br-TIP.

The luminescence spectra of complex **1~3** have been investigated at room temperature by using the same methanol solutions for UV-Vis determination. Although there is no luminescence for **3**, fluorescence emissions of **1** and **2** can be found at λ_{max} =508 and 447 nm upon excitation at λ_{ex} =283 and 277 nm, respectively, as can be seen in Fig.2. Compared with the luminescence emissions of free ligands TIP and 5-Br-TIP, namely 516 and 497 nm in methanol upon

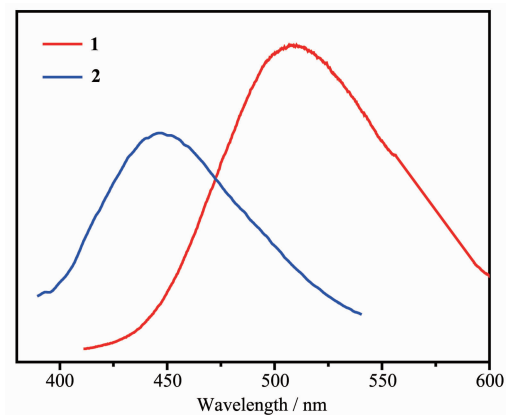


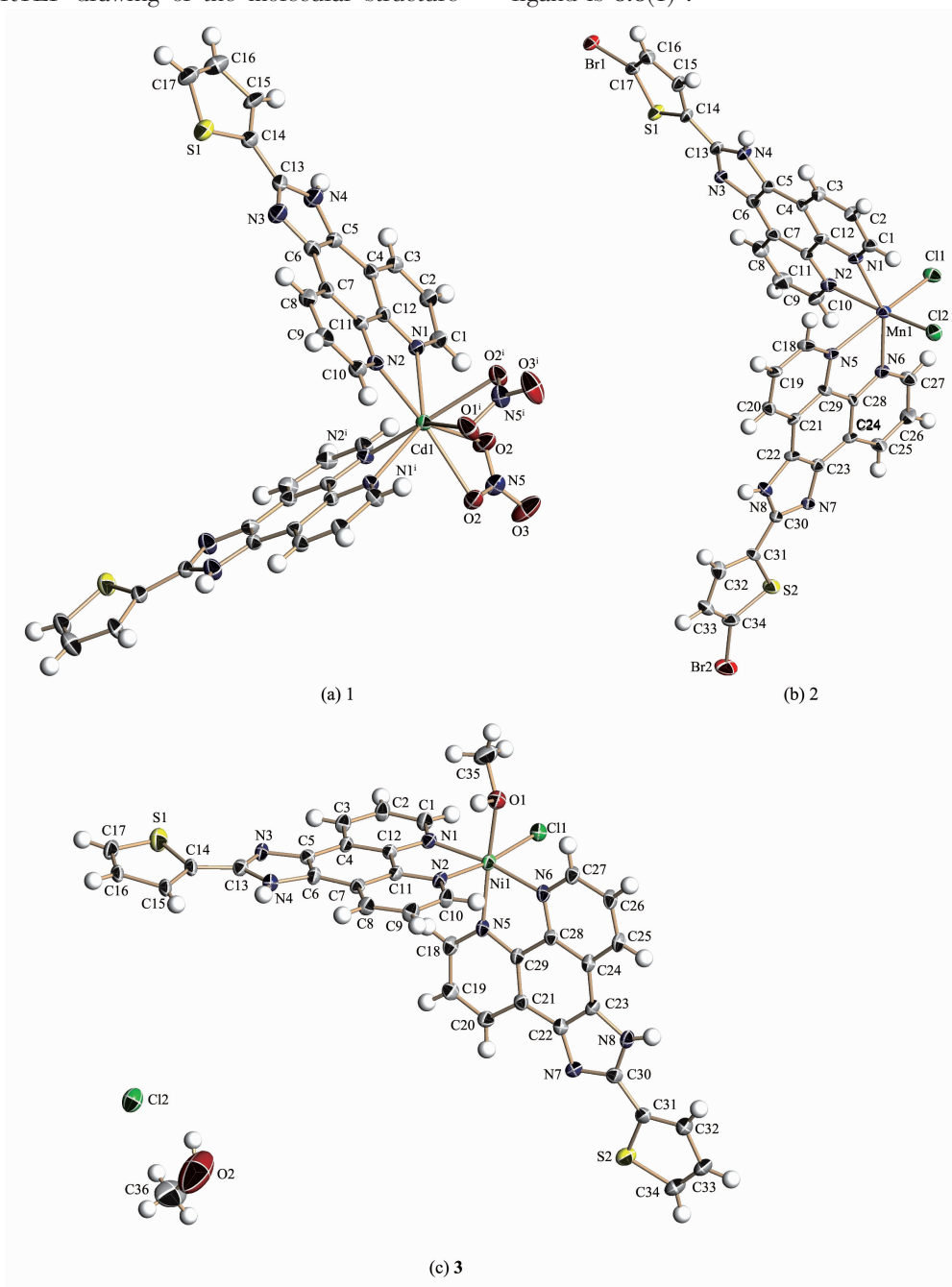
Fig.2 Fluorescence emission spectra of **1** and **2** in CH₃OH at room temperature

excitation at $\lambda_{\text{ex}}=304$ and 340 nm, 8 and 50 nm's blue shifts are observed for **1** and **2** after metal-ion complexation.

2.2 Single-crystal structures of 1:2 mononuclear Cd(II) and Ni(II) complex **1-3**

X-ray single-crystal diffraction analysis for **1** reveals that it crystallizes in the monoclinic space group $C2/c$ and the asymmetric unit contains half of the molecule. ORTEP drawing of the molecular structure

of 1:2 mononuclear Cd(II) complex with the atom-numbering scheme is shown in Fig.3a. The central Cd(II) ion is eight-coordinated by four nitrogen atoms from two chelating TIP ligands and four oxygen atoms from two nitrate anions, respectively. The two chelating TIP ligands and two nitrate anions adopt the cis configuration, and the dihedral angle between the adjacent imidazole and thiophene rings of each TIP ligand is $8.8(1)^\circ$.

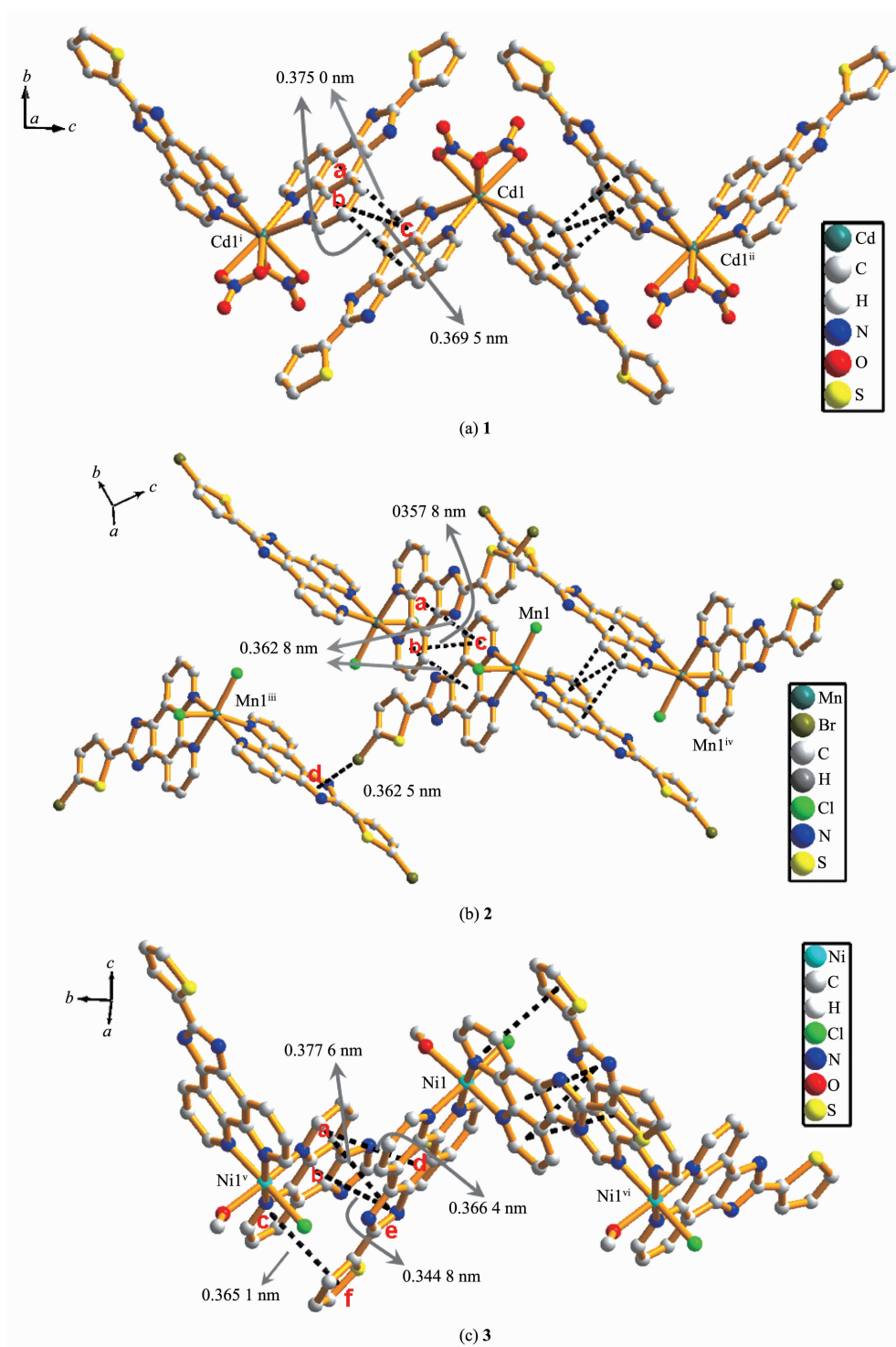


Displacement ellipsoids are drawn at the 30% probability level; Symmetry code in **1**: $1-x, -y, 2-z$

Fig.3 ORTEP diagrams of the molecular structures of **1-3**

As can be seen in Fig.4a, typical offset π - π stacking interactions are found between adjacent molecules in **1**. The central ring and one side ring of phen are found to pack with their counterparts, having the centroid-to-centroid separation of 0.375 0 and

0.369 5 nm, respectively. The former comes from centroid a of one central ring of phen (C4, C5, C6, C7, C11 and C12) and centroid c of its adjacent side aromatic ring of phen (C1, C2, C3, C4, C12 and N1) with the dihedral angle of 1.6(1) $^\circ$, and the latter is



Symmetry codes: ⁱ $-x, 1-y, -z$; ⁱⁱ $-x, 1-y, -z$; ⁱⁱⁱ $3-x, 4-y, -z$; ^{iv} $x, 2+y, z$; ^v $1-x, 1/2+y, 1/2-z$; ^{vi} $1-x, -1/2+y, 1/2-z$

Fig.4 Perspective view of the π - π and p - π stacking interactions in the crystal packing structures of complex **1-3**

between the two neighboring side aromatic rings of phen units [centroid b (also defined from C1, C2, C3, C4, C12 and N1) and centroid c] with the dihedral angle of 0° .

Complex **2** is also a 1:2 mononuclear Mn(II) complex as shown in Fig.3b, and the asymmetric unit consists of one Mn(II) ion, two chelating 5-Br-TIP ligands and two coordinated chlorine anions. It crystallizes in the triclinic space group $P\bar{1}$ and the Mn(II) center is six-coordinated by four nitrogen atoms from two chelating 5-Br-TIP ligands and two chlorine anions, respectively, forming octahedral coordination geometry. The two chelating TIP ligands and two chlorine anions also adopt the cis configuration. The dihedral angles between adjacent imidazole and thiophene rings of the two chelating 5-Br-TIP ligands are $3.9(1)^\circ$ and $5.2(1)^\circ$, respectively, which are smaller than those in the other two complexes in this work.

Offset π - π and p - π stacking interactions are observed in **2** between contiguous molecules as shown in Fig.4b. The central ring and one side ring of phen are found to pack with their counterparts, having the centroid-to-centroid separation of 0.362 8 and 0.357 8 nm, respectively. The former comes from centroid a of one central ring of phen (C4, C5, C6, C7, C11 and C12) and centroid c of its adjacent side aromatic ring of phen (C1, C2, C3, C4, C12 and N1) with the dihedral angle of $1.2(1)^\circ$, and the latter is between the two neighboring side aromatic rings of phen units (centroid b (also defined from C1, C2, C3, C4, C12 and N1) and centroid c) with the dihedral angle of 0° . In addition, p - π stacking interactions are found in **2** between the bromine atom of 5-Br-TIP and its vicinal imidazole ring. The separation between atom Br1 and centroid d (defined from C22, C23, C30, N7 and N8) is measured as 0.362 5 nm.

ORTEP drawing of the molecular structure of 1:2 mononuclear nickel (II) complex **3** with the atom-numbering scheme is shown in Fig.3c. It crystallizes in the monoclinic space group $P2_1/c$ and the central Ni(II) ion is six-coordinated by four nitrogen atoms from two chelating TIP ligands, one chlorine anion

and one oxygen atom from methanol molecule forming six-coordinate octahedral coordination geometry. Different from **2**, there is another uncoordinated chlorine counterion in the asymmetric unit of **3**, together with a methanol molecule. The two chelating TIP ligands and one chlorine anion and one oxygen atom of methanol molecule adopt the same cis configuration as **1** and **2**, and the dihedral angles between adjacent imidazole and thiophene rings of two TIP ligands are $6.5(1)$ and $9.2(1)^\circ$, respectively.

Similarly, offset π - π stacking interactions are observed in **3** between contiguous molecules as shown in Fig.4c. The central ring and one side ring of phen are found to pack with their counterparts, having the centroid-to-centroid separation of 0.377 6 and 0.363 4 nm, respectively. The former comes from centroid e of imidazole ring of TIP (C5, C6, C13, N3 and N4) and centroid a of its adjacent side aromatic ring of phen (C18, C19, C20, C21, C29 and N5) with the dihedral angle of $1.9(1)^\circ$, and the latter is between the central aromatic ring of phen (centroid d defined from C4, C5, C6, C7, C11 and C12) and its contiguous side ring of phen (centroid a) with the dihedral angle of $0.8(2)^\circ$. In addition, π - π stacking interactions are found between centroid e of imidazole ring and its adjacent central ring of phen (centroid b defined from C21, C22, C23, C24, C28 and C29) with the separation of 0.3448 nm and dihedral angle of $3.9(1)^\circ$. Moreover, π - π stacking interactions are observed between centroid c of one side ring of phen (C1, C2, C3, C4, C12 and N1) and its neighboring thiophene ring of TIP (centroid f defined from C14, C15, C16, C17 and S1) with the separation of 0.3651 nm and dihedral angle of $10.3(2)^\circ$.

As far as we are aware, there are only two structural reports up till now on ligands TIP/5-Br-TIP and their metal complexes. One is a Pb(II) complex of ligand TIP^[25] and the other is our contribution on several protonated salts and metal complexes of ligands TIP and 5-Br-TIP including two dinuclear and planar complexes with the whole molecular lengths of 2.52 and 2.90 nm^[24h].

3 Conclusions

In summary, two 5,6-extended 1,10-phenanthroline-based heterocyclic aromatic ligands (TIP and 5-Br-TIP) are used to prepare three new mononuclear transition-metal complex **1~3** with the same metal/ligand molar ratio of 1:2 and *cis* configuration. Ligands TIP and 5-Br-TIP are essentially planar in complex **1~3** with the dihedral angles between imidazole and thiophene rings in the range of 3.9(1)°~9.2(1)°, and abundant supramolecular interactions, such as π - π , *p*- π stacking and hydrogen bonding, have been observed in their crystal packing structures.

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