

3,8-二噻吩和 3,8-二甲基噻吩-1,10-菲啰啉的锰(II)和钴(II) 配合物的晶体结构、顺反异构及取代基效应研究

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摘要: 本文报道了 1 个基于 3,8-二噻吩-1,10-菲啰啉(dtpen) 的双核锰(II)配合物 **1** [*trans*-Mn₂Cl₄(dtpen)₂] 和 2 个基于 3,8-二甲基噻吩-1,10-菲啰啉(dmtphen)的单核锰(II)和单核钴(II)配合物 **2** 和 **3** (分子式分别为 [*cis*-MnCl₂(dmtphen)₂] 和 [*cis*-CoCl₂(dmtphen)₂]) 的合成、波谱和晶体结构表征。其中, 2 个锰(II)配合物的分子结构呈现不同的配位模式, 由于噻吩环上甲基引入所产生的位阻效应, 导致单核配合物 **2** 和 **3** 中, 两配体中的噻吩环相对于 1,10-菲啰啉呈现相同的反式/反式分子构型, 其二面角分布在 14.1(1)°~51.5(1)°。而对于双核配合物 **1**, 由于没有甲基位阻的影响, 其相应芳环之间二面角减少至 2.0(1)°~20.2(1)°, 且配体呈现顺式/反式分子构型。

关键词: 锰(II)配合物; 钴(II)配合物; 取代基效应; 顺反异构; 晶体结构

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Synthesis, Crystal Structures, *Cis-Trans* Conformation and Substituent Effects of Manganese(II) and Cobalt(II) Complexes Having 3,8-Dithiophen or 3,8-Di-3-methylthiophen-1,10-phenanthroline

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Abstract: A dinuclear 3,8-dithiophen substituted 1,10-phenanthroline (dtpen) manganese(II) complex and a pair of 3,8-di-3-methylthiophen substituted 1,10-phenanthroline (dmtphen) manganese(II) and cobalt(II) complexes, formulated as [*trans*-Mn₂Cl₄(dtpen)₂] (**1**), [*cis*-MnCl₂(dmtphen)₂] (**2**) and [*cis*-CoCl₂(dmtphen)₂] (**3**), were synthesized and characterized by elemental analysis, FTIR, UV-Vis spectra and X-ray single-crystal structural analysis. The two Mn(II) complexes exhibit diverse coordination models in the whole molecular structures. In mononuclear complexes **2** and **3**, both dmtphen ligands have similar *trans/trans* conformation but different dihedral angles ranging from 14.1(1)°~51.5(1)° because of the spatial crowding effects of methyl group. In contrast, the dihedral angles of dtpen ligands in dinuclear complex **1** are only within 2.0(1)°~20.2(1)° and the two side thiophene rings in the dtpen ligand adopt the *cis/trans* conformation relative to the central phen unit. CCDC: 870021, **1**; 870022, **2**; 870023, **3**.

Key words: manganese(II) complexes; cobalt(II) complexes; substituent effects; *cis* and *trans* configuration; crystal structure

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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^[6-7], organic field-effect transistors^[8], organic light-emitting diodes^[9-11], and molecular nanowires^[12]. In this field, 1,10-phenanthroline derivatives are interesting organic semiconducting precursors due to their strong chelating abilities and good conjugated π systems. At the same time, the coordination conformation and chemical structures of metal complexes having 1,10-phenanthroline derivatives can be finely adjusted by introducing diverse organic functional groups at 2,9,3,8, and 5,6 positions of 1,10-phenanthroline as well as other auxiliary ligands^[13].

Studies on the relationship between the interactions in supramolecular level and the molecular conformation such as *cis/trans* isomerism seem to be very interesting and important, because many of potential characters and applications related to the *cis* and *trans* conformation have been involved in various subjects ranging from inorganic^[14] to organic and biological chemistry. For example, *cis*-[(NH₃)₂PtCl₂] has been widely used as an anti-cancer drug, while *trans*-[(NH₃)₂PtCl₂] shows no anti-cancer activity.

In our previous work, we have successfully constructed a family of linear 1,10-phenanthroline

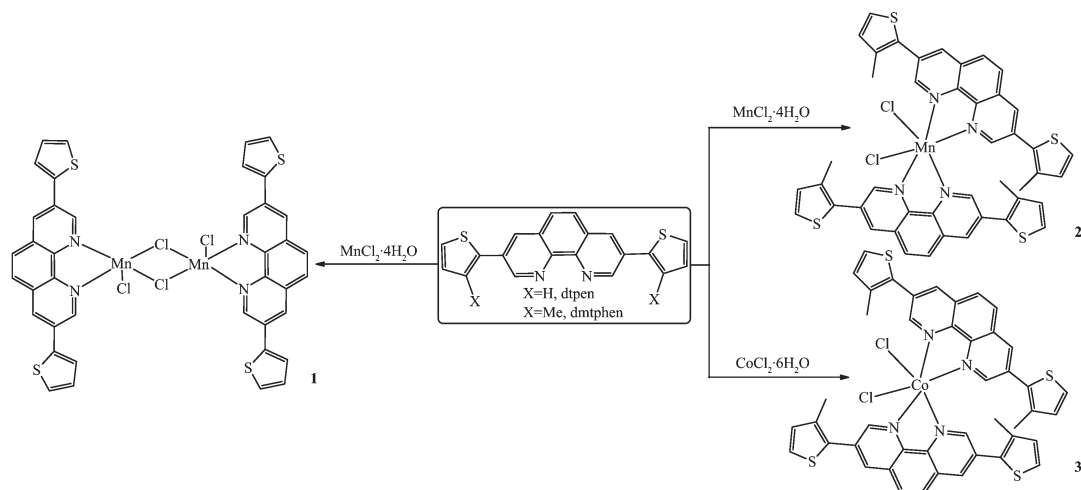
extended heterocyclic aromatic fluorescence semi-conducting compounds by introducing a groups of thiophene, imidazole, pyridyl, phenyl and oligothiophene units into the 3 and 8 positions of 1,10-phenanthroline via the carbon-carbon and carbon-nitrogen crossing coupling reactions^[15-19]. Recently we have reported four nickel(II), zinc(II), and copper(II) perchlorate metal complexes of 3,8-di (thiophen-2',2''-yl)-1,10-phenanthroline (dtphen) with different metal-to-ligand ratios^[20]. In this contribution, we use dtphen to prepare its manganese(II) chloride complex [*trans*-Mn₂Cl₄ (dtphen)₂] (**1**) and make comparisons with similar 3,8-di(3-methylthiophen-2-yl)-1,10-phenanthroline (dmtphen) based manganese(II) and cobalt(II) chloride complexes [*cis*-MnCl₂(dmtphen)₂] (**2**) and [*cis*-CoCl₂ (dmtphen)₂] (**3**), in order to investigate how the substituent and anionic effects affect the conformation of ligands as well as final metal complexes (Scheme 1).

1 Experimental

1.1 Materials and instruments

All reagents and solvents were of analytical grade and used without any further purification. The anhydrous solvents were drawn into syringes under a flow of dry N₂ gas and directly transferred into the reaction flask to avoid contamination. 3,8-Dibromo-1,10-phenanthroline^[21], dtphen^[22] and dmtphen^[19] were prepared via previously reported approaches.

Elemental analyses (EA) for carbon, hydrogen,



Scheme 1 Schematic illustration for the preparation of metal complex **1**, **2** and **3**

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 Pyrex cell with a path length of 10 mm.

1.2 Synthesis of the compounds

Preparation of complex **1**: [*trans*- $\text{Mn}_2\text{Cl}_4(\text{dtphen})_2$] (**1**): A solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (9.8 mg, 0.05 mmol) in methanol (5 mL) was added dropwise to a solution of dtphen (34.4 mg, 0.1 mmol) in methanol (5 mL). After stirred and refluxed for 3 h, the mixture was cooled and filtered, and the filtrate was left for slow evaporation in air at room temperature. Pale-yellow block single crystals of **1** suitable for X-ray crystallographic analysis were obtained after one week. Yield: 3.5 mg (14.9 % based on metal). Main FTIR absorptions (KBr pellets, ν/cm^{-1}): 3 442 (b), 1 604 (m), 1 529 (w), 1 506 (w), 1 438 (vs), 1 390 (w), 1 346 (w), 1 270 (w), 1 118 (w), 1 070 (w), 1 041 (w), 916 (m), 885 (w), 846 (m), 781 (w), 714 (s), 526 (w). Elemental Anal. Calcd. for $\text{C}_{40}\text{H}_{24}\text{Cl}_4\text{Mn}_2\text{N}_4\text{S}_4$ (%): C 51.08; N 5.96; H 2.57. Found (%): C 51.34; N 5.67; H 2.83. UV-Vis in methanol: λ_{max} =366, 354, 284, and 218 nm.

[*cis*- $\text{MnCl}_2(\text{dmtphen})_2$] (**2**): The preparation of **2** is similar to that of **1** except that dmtphen (37.2 mg, 0.1 mmol) was used instead of dtphen. Yellow block single crystals of **2** suitable for X-ray crystallographic analysis were obtained after one week. Yield: 14.6 mg (33.5 % based on metal). Main FTIR absorptions (KBr pellets, ν/cm^{-1}): 3 440 (b), 2 360 (m), 2 343 (w), 1 603 (m), 1 539 (w), 1 439 (vs), 1 351 (w), 1 263 (w), 1 122 (m), 1 022 (w), 916 (w), 727 (s), 707 (w). Elemental Anal. Calcd. for $\text{C}_{44}\text{H}_{32}\text{Cl}_2\text{MnN}_4\text{S}_4$ (%): C 60.68; N 6.43; H 3.70. Found (%): C 60.87; N 6.24; H 3.83. UV-Vis in methanol: λ_{max} =348, 282, 252, and 226 nm.

[*cis*- $\text{CoCl}_2(\text{dmtphen})_2$] (**3**): **3** was prepared in the same method as that of **2** except that $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (11.9 mg, 0.05 mmol) was used instead of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Red block single crystals of **3** suitable for X-ray crystallographic analysis were obtained after one week. Yield: 20.3 mg (46.4% based on metal). Main

FT-IR absorptions (KBr pellets, ν/cm^{-1}): 3 442 (b), 1 598 (m), 1 536 (w), 1 506 (w), 1 473 (w), 1 439 (vs), 1 379 (m), 1 351 (m), 1 319 (w), 1 265 (w), 1 122 (m), 1 022 (w), 914 (m), 883 (w), 837 (w), 779 (w), 727 (s), 708 (s), 629 (w). Elemental Anal. Calcd. for $\text{C}_{44}\text{H}_{32}\text{Cl}_2\text{CoN}_4\text{S}_4$ (%): C 60.41; N 6.40; H 3.69. Found(%): C 60.62; N 6.53; H 3.46. UV-Vis in methanol: λ_{max} =366, 292, 255, and 224 nm.

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 $K\alpha$ radiation (λ =0.071 073 nm). The crystal systems were determined by 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^2 by using the SHELXTL-PC software package^[23-25]. 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 complexes **1~3** is listed in Table 1, while selected bond distances and bond angles related to the central Mn(II) and Co(II) ions are given in Table 2. Hydrogen bonding interactions in complexes **1~3** are shown in Table 3.

CCDC: 870021, **1**; 870022, **2**; 870023, **3**.

2 Results and discussion

2.1 Synthesis and spectral characterizations

Two manganese(II) and one cobalt(II) complexes **1~3** can be easily prepared just by refluxing stoichiometric manganese(II) chloride or cobalt(II) chloride with dtphen or dmtphen in methanol for 3 h. The formation of stable, neutral and divalent metal complexes can be verified by their elemental and FTIR spectral analyses. Furthermore, UV-Vis spectra of complexes **1~3** in methanol are illustrated in Fig.1.

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

Complex	1	2	3
Empirical formula	C ₄₀ H ₂₄ Cl ₄ MnN ₄ S ₄	C ₄₄ H ₃₂ Cl ₂ MnN ₄ S ₄	C ₄₄ H ₃₂ Cl ₂ CoN ₄ S ₄
Formula weight	940.59	870.86	874.85
Crystal size / mm	0.10×0.11×0.12	0.10×0.10×0.12	0.10×0.11×0.12
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> / nm	0.949 7(2)	1.194 3(1)	1.174 1 (1)
<i>b</i> / nm	0.963 2(2)	1.266 7(1)	1.271 9 (1)
<i>c</i> / nm	1.134 1(3)	1.444 4(2)	1.446 6(1)
α / (°)	70.024(3)	95.660(2)	96.256(1)
β / (°)	88.831(4)	100.078(2)	99.621(1)
γ / (°)	76.705(3)	106.077(2)	106.038(1)
<i>V</i> / nm ³	0.947 0(4)	2.042 0(4)	2.019 4(3)
<i>Z</i>	1	2	2
<i>D_c</i> / (g·cm ⁻³)	1.649	1.416	1.439
<i>F</i> (000)	474	894	898
μ (Mo <i>K</i> α) / mm ⁻¹	1.207	0.696	0.802
Max. / min. transmission	0.888 8 / 0.868 7	0.933 6 / 0.921 1	0.924 1 / 0.909 9
Limiting indices	-11 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 11, -13 ≤ <i>l</i> ≤ 8	-14 ≤ <i>h</i> ≤ 14, -7 ≤ <i>k</i> ≤ 15, -17 ≤ <i>l</i> ≤ 17	-13 ≤ <i>h</i> ≤ 10, -15 ≤ <i>k</i> ≤ 15, -17 ≤ <i>l</i> ≤ 17
Parameters	245	500	500
Reflections collected	4 832	10 440	10 285
Independent reflections (<i>R</i> _{int})	3 294 (0.050 4)	7 093 (0.049 9)	6 998 (0.033 7)
Observed reflections (<i>I</i> > 2 σ (<i>I</i>))	2 206	3 074	4 281
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.043 8, 0.104 6	0.079 0, 0.167 6	0.069 6, 0.196 8
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.070 4, 0.120 0	0.153 9, 0.193 3	0.106 8, 0.221 3
Goodness of fit on <i>F</i> ²	0.963	0.984	1.000
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ / (e·nm ⁻³)	517, -459	1 416, -924	1 219, -758

Table 2 Selected bond distances (nm) and angles (°) for complex 1~3

1					
Mn1-N1	0.221 2(3)	Mn1-Cl1	0.233 4(1)	Mn1-Cl2i	0.244 9(1)
Mn1-N2	0.227 0(3)	Mn1-Cl2	0.256 1(1)		
Cl1-Mn1-Cl2 ⁱ	106.5(1)	N2-Mn1-Cl1	98.4(1)	N2-Mn1-Cl2 ⁱ	94.3(1)
Cl2-Mn1-Cl2 ⁱ	86.9(1)	N1-Mn1-Cl2	89.1(1)	Cl1-Mn1-Cl2	104.4(1)
N1-Mn1-N2	74.5(1)	N1-Mn1-Cl2 ⁱ	140.1(1)		
N1-Mn1-Cl1	112.9(1)	N2-Mn1-Cl2	155.8(1)		
2					
Mn1-N1	0.237 1(6)	Mn1-N3	0.226 0(5)	Mn1-Cl1	0.240 6(3)
Mn1-N2	0.227 1(6)	Mn1-N4	0.235 6(6)	Mn1-Cl2	0.242 4(2)
N3-Mn1-Cl2	96.2(2)	N1-Mn1-N3	86.4(2)	N1-Mn1-Cl1	163.1(2)
N4-Mn1-Cl1	88.2(2)	N1-Mn1-N4	79.8(2)	N1-Mn1-Cl2	88.9(2)
N4-Mn1-Cl2	163.8(2)	N2-Mn1-N3	154.1(2)	N2-Mn1-Cl1	97.4(2)

Continued Table 2

Cl1-Mn1-Cl2	105.1(1)	N2-Mn1-N4	91.2(2)	N2-Mn1-Cl2	96.2(2)
N1-Mn1-N2	71.2(2)	N3-Mn1-N4	71.7(2)	N3-Mn1-Cl1	101.2(2)
3					
Co1-N1	0.215 2(4)	Co1-N3	0.220 9(4)	Co1-Cl1	0.237 1(2)
Co1-N2	0.220 1(4)	Co1-N4	0.214 0(4)	Co1-Cl2	0.239 0(2)
N3-Co1-Cl2	89.5(1)	N1-Co1-N3	90.5(2)	N1-Co1-Cl1	97.1(1)
N4-Co1-Cl1	95.0(1)	N1-Co1-N4	164.6(2)	N1-Co1-Cl2	95.6(1)
N4-Co1-Cl2	91.4(1)	N2-Co1-N3	83.1(2)	N2-Co1-Cl1	87.7(1)
Cl1-Co1-Cl2	100.9(1)	N2-Co1-N4	94.6(2)	N2-Co1-Cl2	169.1(1)
N1-Co1-N2	76.5(2)	N3-Co1-N4	75.8(2)	N3-Co1-Cl1	166.4(1)

Symmetry code: ⁱ 1-x, -y, 2-z for **1**.

Table 3 Hydrogen bonding interactions in complexes 1~3

D-H...A	d(D-H) / nm	d(H...A) / nm	d(D...A) / nm	∠DHA / (°)
1				
C6-H6...Cl1 ⁱⁱ	0.093	0.278	0.356 8(5)	144
Cl3-H13...Cl1 ⁱⁱⁱ	0.093	0.281	0.355 7(6)	138
2				
C22-H22...Cl2 ⁱ	0.093	0.275	0.365 1(12)	165
C47-H27...Cl1 ⁱⁱ	0.093	0.274	0.362 1(8)	157
3				
C5-H5...Cl1 ⁱ	0.093	0.272	0.358 0(7)	154
C44-H44...Cl2 ⁱⁱ	0.093	0.275	0.366 1(9)	166

Symmetry codes: ⁱⁱ 1-x, 1-y, 1-z; ⁱⁱⁱ -x, 1-y, 2-z for **1**; ⁱ -1+x, y, z; ⁱⁱ 2-x, 1-y, 1-z for **2**; ⁱ 2-x, 1-y, 1-z; ⁱⁱ -1+x, y, z for **3**.

Compared with the absorptions of two free ligands, the π - π^* transition between the heterocyclic aromatic rings shows a bathochromic shift from 352 nm in ligand dtphen^[19] to 367 nm in its dinuclear Mn(II) complex **1** and a slightly hypsochromic shift from 351 nm to 348 nm in its mononuclear Mn(II) complex **2**. In contrast, absorption of the π - π^* transition between the aromatic heterorings is also slightly red-shifted

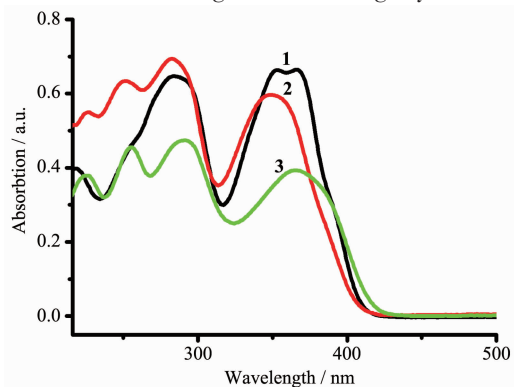


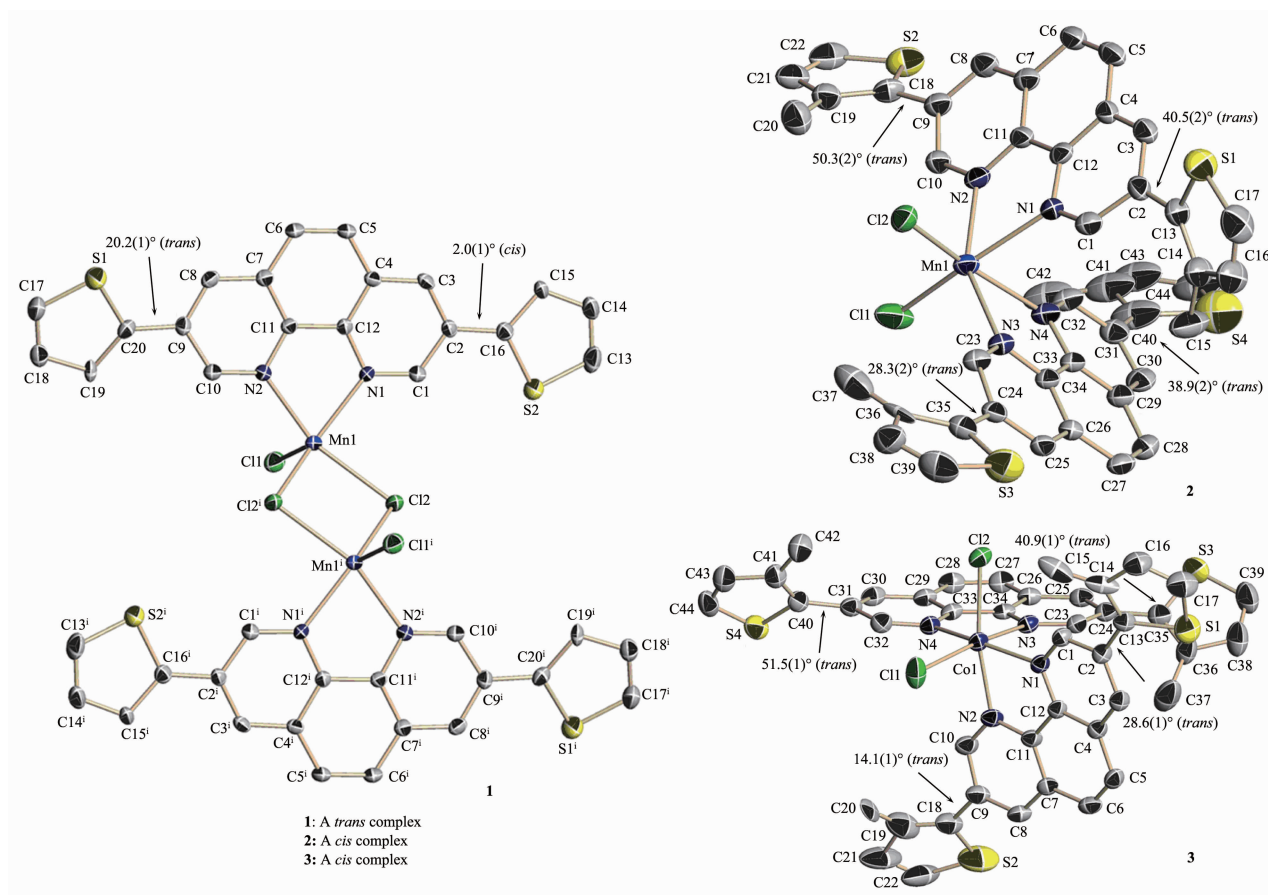
Fig.1 UV-Vis spectra of complexes 1~3 in methanol at room temperature

from 351 nm in ligand dmtphen to 366 nm in its mononuclear Co(II) complex **3**.

2.2 Single-crystal structure of the dinuclear Mn(II) complex 1

As shown in Fig.2, X-ray single-crystal structural determination of complex **1** reveals that it crystallizes in the triclinic $P\bar{1}$ space group in which a crystallographically imposed center of symmetry is observed. The central Mn(II) ion is five-coordinated by two nitrogen atoms (N1 and N2) from one bidentate dtphen ligand, two μ_2 -Cl⁻ ions (Cl2 and Cl2ⁱ) in the equatorial plane and one Cl⁻ counterion (Cl1) in the axial position to form a distorted pyramidal coordination environment as indicated by an index τ value of 0.262^[26]. The three measured Mn-Cl bond lengths are 0.233 4(1), 0.256 1(1), 0.244 9(1) nm and two Mn-N ones are 0.221 2(3) and 0.227 0(3) nm, respectively (Table 2).

Two Mn(II) ions were connected by two μ_2 -Cl⁻ atoms to form a dinuclear complex in **1**. Furthermore,



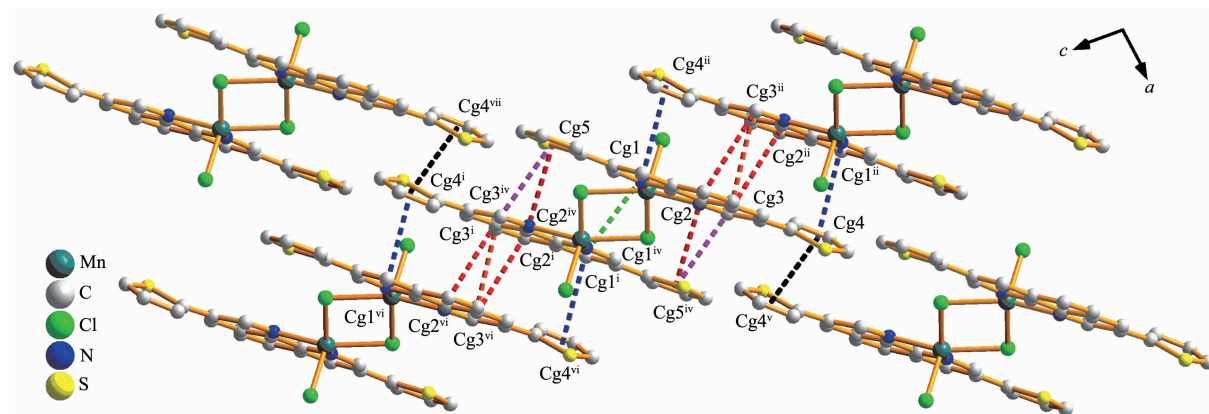
Hydrogen atoms are omitted for clarity and displacement ellipsoids are drawn at the 30% probability level; Symmetry codes: ⁱ 1-x, -y, 2-z for **1**

Fig.2 ORTEP diagrams of molecular structures of metal complexes **1~3**

two chelating dtphen ligands and two apical Cl⁻ counterions adopt the trans configuration with regard to the whole complex. At the same time, the two side thiophene rings of ligands dtphen in **1** adopt the *cis/trans* conformation relative to the central 1,10-phenanthroline unit. The dihedral angles between the S1 and S2 located thiophene rings and their mother

1,10-phenanthroline rings are 2.0 (1)° and 20.2 (1)°, respectively.

It is noteworthy that there are abundant π - π stacking interactions in the packing structure of **1** between the neighboring aromatic heterorings, and the centroid-to-centroid distances between adjacent heterorings are in the range of 0.366 3(6)~0.387 7(6) nm.



Symmetry codes: ⁱ 1-x, -y, 2-z, ⁱⁱ 1-x, 1-y, 1-z, ^{iv} 1-x, 1-y, 2-z, ^v 2-x, -y, 1-z, ^{vi} x, -1+y, 1+z, ^{vii} -1+x, y, 1+z

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

As can be seen in Fig.3, by virtue of these π - π stacking interactions, complex **1** is extended into a three-dimensional supramolecular network which will significantly stabilize its solid-state structure.

2.3 Single-crystal structures of mononuclear Mn(II) and Co(II) complexes **2** and **3**

The X-ray single-crystal diffraction analyses for complexes **2** and **3** show that they are mononuclear complexes and they both crystallize in the triclinic space group of $P\bar{1}$. The coordination geometry around the central Mn(II) and Co(II) ions can be described as a six-coordinate distorted octahedron by four nitrogen atoms (N1, N2, N3 and N4) from two bidentate dmtphen ligands and two Cl⁻ counterions (Cl1 and Cl2). Although **2** and **3** are polymorphous structures and both of the dmtphen ligands adopt the trans/trans conformation, the dihedral angles of two ligands are slightly different. In complex **2**, the dihedral angles between adjacent aromatic heterorings are 40.5(2)°, 50.3(2)°, 28.3(2)°, and 38.9(2)° (S1, S2, S3, and S4 located), respectively. In complex **3**, the dihedral

angles between adjacent aromatic heterorings are 28.6(1)°, 14.1(1)°, 40.9(1)°, and 51.5(1)° (S1, S2, S3, and S4 located), respectively. All these dihedral angles are larger than those in complex **1**. The differences in the dihedral angles between adjacent aromatic heterorings in complexes **1**~**3** are believed to originate from the spatial crowding effects of methyl group in ligand dmtphen.

It is interesting to note that two Cl⁻ ions in complexes **2** or **3** have different coordination mode compared with that of complex **1**, both of them are monodentate linking the same metal centers to form a mononuclear complex. The measured Mn-N bond lengths are 0.236 9(6), 0.227 5(6), 0.225 9(6) and 0.235 4(7) nm in **2**, while the Co-N bond lengths are slight shorter in the range from 0.214 0(4) to 0.220 9(4) nm (Table 2). In contrast, the Mn-Cl bond lengths in **2** are 0.240 9(3) and 0.242 4(2) nm, while the Co-Cl bond lengths in **3** are 0.237 1(2) and 0.239 0(2) nm, indicative of the different radii of coordination atoms (Cl versus N) and metal ions (Mn²⁺ versus Co²⁺).

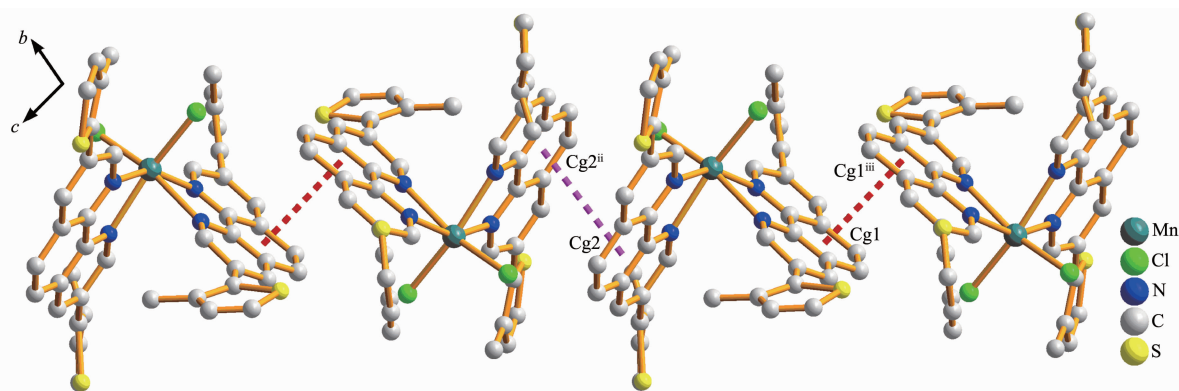


Fig.4 Perspective view of the π - π stacking interactions in the crystal packing of complex **2**

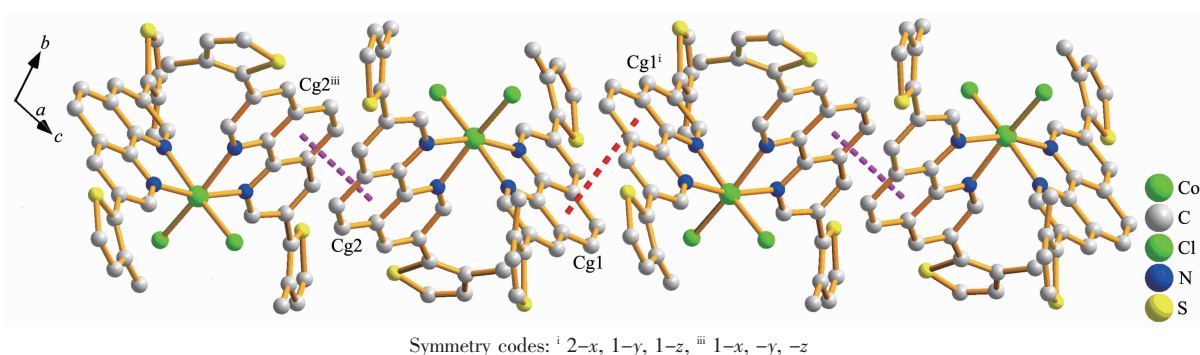


Fig.5 Perspective view of the π - π stacking interactions in the crystal packing of complex **3**

In the crystal packing structures of complexes **2** and **3**, π - π stacking interactions are also observed between the central phenyl rings of neighboring phenanthroline planes. The centroid-to-centroid separations are 0.350 4(12) and 0.400 4(12) nm in **2**, and those between adjacent phenyl rings are 0.347 7(8) and 0.397 3(8) nm in **3**. As a result, two one-dimensional supramolecular chains are formed by the intermolecular π - π stacking interactions, as shown in Fig.4 and Fig. 5, respectively.

3 Conclusions

In summary, dtphen and dmtphen ligands are used to prepare two new manganese(II) and one cobalt(II) complexes **1~3** with different nuclearities for comparison. They have diverse coordination structures where substituent and anionic effects on the final *cis/trans* configuration of ligands and metal complexes are explored. As for the dinuclear Mn(II) complex **1**, the central metal ion is five-coordinated showing the *cis* conformation, while the central metal ions of mononuclear Mn(II) and Co(II) complexes **2** and **3** are six-coordinated exhibiting the *trans* configuration. Moreover, the slight difference in the dtphen and dmtphen molecules results in the distinguishing dihedral angles between adjacent aromatic rings in ligands as well as the alteration of *cis* and *trans* conformation with regard to the whole complexes, mainly due to the substituent and anionic effects. According to this study, it is suggested that diverse coordination conformation and interesting molecular architectures can be achieved through the adjustment of substituent, steric, π - π stacking and hydrogen bonding interactions.

References:

- [1] Liu B, Bazan G C. *Chem. Mater.*, **2004**,**16**(23):4467-4476
- [2] Xue X J, Wang F, Liu X G. *J. Am. Chem. Soc.*, **2008**,**130**(11):3244-3245
- [3] McQuade D T, Pullen A E, Swager T M. *Chem. Rev.*, **2000**, **100**(7):2537-2574
- [4] Thomas S W, Joly G D, Swager T M. *Chem. Rev.*, **2007**,**107**(4):1339-1386
- [5] McGehee M D, Heeger A J. *Adv. Mater.*, **2000**,**12**(22):1655-1668
- [6] Chen C Y, Wang M K, Li J Y, et al. *ACS Nano.*, **2009**,**3**(10):3103-3109
- [7] Hara K, Sato T, Katoh R, et al. *Adv. Funct. Mater.*, **2005**,**15**(2):246-252
- [8] Wu W P, Liu Y Q, Zhu D B. *Chem. Soc. Rev.*, **2010**,**39**(5):1489-1502
- [9] Gross M, Muller D C, Nothofer H G, et al. *Nature*, **2000**, **405**(6787):661-665
- [10] Kulkarni A P, Tonzola C J, Babel A, et al. *Chem. Mater.*, **2004**,**16**(23):4556-4573
- [11] Lo S C, Burn P L. *Chem. Rev.*, **2007**,**107**(4):1097-1116
- [12] Zang L, Che Y K, Moore J S. *Accounts Chem. Res.*, **2008**, **41**(12):1596-1608
- [13] Bencini A, Lippolis V. *Coord. Chem. Rev.*, **2010**,**254**(17-18):2096-2180
- [14] Melnik M, Holloway C E. *Coord. Chem. Rev.*, **2006**,**250**(17-18):2261-2270
- [15] Huang W, Tanaka H, Ogawa T. *J. Phys. Chem. C*, **2008**,**112**(30):11513-11526
- [16] Huang W, Masuda G, Maeda S, et al. *Inorg. Chem.*, **2008**, **47**(2):468-480
- [17] Wang L, You W, Huang W, et al. *Inorg. Chem.*, **2009**,**48**(10):4295-4305
- [18] Huang W, Tanaka H, Ogawa T, et al. *Adv. Mater.*, **2010**,**22**(25):2753-2758
- [19] Hu B, Fu S J, Xu F, et al. *J. Org. Chem.*, **2011**,**76**(11):4444-4456
- [20] Hu B, Xu F, Fu S J, et al. *Inorg. Chim. Acta*, **2010**,**363**(7):1348-1354
- [21] Saitoh Y, Koizumi T, Osakada K, et al. *Can. J. Chem.-Rev. Can. Chim.*, **1997**,**75**(10):1336-1339
- [22] Araki K, Endo H, Masuda G, et al. *Chem.-Eur. J.*, **2004**,**10**(13):3331-3340
- [23] Siemens, *SAINT v4 Software Reference Manual*, Siemens Analytical X-Ray Systems, Inc., Madison, Wisconsin, USA, **2000**.
- [24] Sheldrick G M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, Univ. of Gottingen, Germany, **2000**.
- [25] Sheldrick G M. *SHELXTL, Version 6.10 Software Reference Manual*, Siemens Analytical X-Ray Systems, Inc., Madison, Wisconsin, USA, **2000**.
- [26] Addison A W, Rao T N, Reedijk J, et al. *J. Chem. Soc. Dalton Trans.*, **1984**(7):1349-1356