# 手性配体 2,5-二(4,5-蒎烯-2-吡啶)吡嗪及其铼配合物的合成与表征

李书静 [1,2]　张小朋 [1]　刘　建 [1]　郑　玮 [1]　李承辉 [*,1]

([1] 南京大学化学化工学院,配位化学国家重点实验室,南京微结构国家实验室,南京　210093)
([2] 周口师范学院化学系,周口　466000)

**摘要:** 本文报道了手性配体 2,5-二(4,5-蒎烯-2-吡啶)吡嗪(L)及其铼配合物[Re(CO)₃Cl(L)]·DMF 的合成与表征。X 射线单晶衍射分析表明配体 L 晶体为单斜 $P2_1$ 空间群,而配合物[Re(CO)₃Cl(L)]·DMF 晶体为正交 $P2_12_12_1$ 空间群。配合物[Re(CO)₃Cl(L)]·DMF 中铼原子与配体中的 2 个氮原子、3 个羰基中的碳原子以及 1 个氯原子配位。CD 谱和 VCD 谱测试表明,配体和配合物都表现出光学活性。受光激发时,配体和配合物分别在 420 和 650 nm 处发光。配体和配合物都具有二阶非线性光学性质,其二阶非线性光学效应分别为尿素的 0.4 和 0.3 倍。

**关键词:** 蒎烯;铼配合物;发光;手性;圆二色谱

**中图分类号:** O614.71⁺³　　**文献标识码:** A　　**文章编号:** 1001-4861(2013)08-1745-08
**DOI:** 10.3969/j.issn.1001-4861.2013.00.295

# Synthesis and Characterization of Chiral 2,5-Bis(4,5-pinene-2-pyridyl) Pyrazine and Its Rhenium(I) Complex

LI Shu-Jing[1,2]　　ZHANG Xiao-Peng[1]　　LIU Jian[1]　　ZHENG Wei[1]　　LI Cheng-Hui[*,1]

([1]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering,
Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China)
([2]Department of Chemistry, Zhoukou Normal University, Zhoukou, Henan 466000, China)

**Abstract:** The chiral ligand 2,5-bis(4,5-pinene-2-pyridyl) pyrazine (L) and its rhenium(I) complex [Re(CO)₃Cl(L)]·DMF were synthesized. X-ray crystallographic analysis show that L crystallizes in monoclinic $P2_1$ space group while [Re (CO)₃Cl (L)]·DMF crystallizes in orthorhombic $P2_12_12_1$ space group. The Re(I) atom is six-coordinated by two nitrogen atoms (N1, N2) from the chiral ligand, three carbon atoms (C1, C2 and C3) from CO, and one chlorine atom (Cl1). Both ligand and [Re(CO)₃Cl(L)]·DMF show optical activity as manifested by the CD and VCD spectra. Upon excitation, the ligand and Re(I) complex emit at 420 and 650 nm, respectively. Both the ligand and Re(I) complex show second-order non-linear optic (NLO) properties, and the second harmonic generation (SHG) responses are ~0.4 and ~0.3 times that of urea, respectively. CCDC: 921976, complex; 921977, ligand.

**Key words:** pinene; rhenium(I) complex; luminescence; chiral; circular dichlorism

　　Recently, the investigation of chiral coordination compounds has been a popular topic owing to their intriguing architectures and topologies, as well as potential applications in asymmetric catalysis, enan-tioselective separations, biomimetic chemistry, nonlinear optical materials, and ferroelectric materials [1-7]. Compared to chiral organic compounds which have been intensively investigated several decades ago, the

chirality of coordination compounds is much more complex due to the various possible coordination geometries of metal centers, which lead to an enormous number of possible configurations in coordination complexes and make stereoselective-synthesis of coordination species a formidable task. The classical method for the preparation of an enantiopure substance is the separation of a racemate. Obviously, this method is only practicable if the number of isomers is rather less, and even then it is often of limited efficiency, and less yield. A more straightforward and effective strategy to construct chiral coordination complexes is using an optically pure chiral organic ligand as a linker to connect adjacent metal centers. In this way, a predetermination of the absolute configuration at the metal center can be reached[8-11].

Pinene is a rigid, bulky group and has been widely used as chiral source in synthesizing chiral compounds[12-14]. Meanwhile, the combination of pinene with pyridine moiety leads to ideal binding ligands toward various metals. Some of them have been widely used in self-assembly and stepwise complexation reactions, giving rise to racemic or configurationally undefined products. For example, Rich et al [15] described a series of mononuclear and dinuclear chiral manganese(II) complexes containing the neutral bidentate chiral nitrogen ligand (−)-pinene[5,6]bipyridine, which showed good selectivities and moderate enantioselectivities in the epoxidation of aromatic alkenes with peracetic acid. Mamula and coworks [16] reported a trinuclear Eu(III) complex formed by chiral bipyridine-carboxylate ligand, which displayed a very interesting mode of helical chirality that originated from the propeller-like arrangement of the ligands around the trinuclear metal core.

Due to the tunable photophysical properies and good chemical stability, Re(I) complexes have attracted more and more attention, and some of them have been used for solar-energy conversion, luminescent bio-labeling, and DNA probes. Yi et al[17] studied the photophysical properties of rhenium (I) tricarbonyl polypyridine complexes and observed an upconversion

quantum yield up to 17.0%. Oriskovich et al[18] reported that the complex Re(bpy)(CO)$_3$(EtG)$^+$ could be used as luminescent labels for purine nucleobases. Esteves et al[19] investigated the interaction of tricarbonyl rhenium (I) complexes with calf thymus DNA (CT-DNA). However, the investigation of structures and properties of chiral rhenium (I) complexes is still limited. Yeung et al[20] synthesized a series of single-stranded helical Re (I) complexes by reacting [Re(CO)$_5$Br] with chiral pinene-containing quaterpy-ridine ligands, in which the chiral information was transmitted from the ligand, through the metal, to the helix, just like in many biomolecules such as R-helix and single-stranded RNA. In this work, we used the 2,5-bis(4,5-pinene-2-pyridyl) pyrazine (L) to construct the organic-inorganic compound [Re(CO)$_3$Cl(L)]·DMF (Scheme 1). The structure of the Re(I) complex was characterized by single crystal X-ray diffraction. The UV, PL, CD and VCD spectra, and non-linear optical properties of the ligand and the Re(I) complex were investigated and compared.
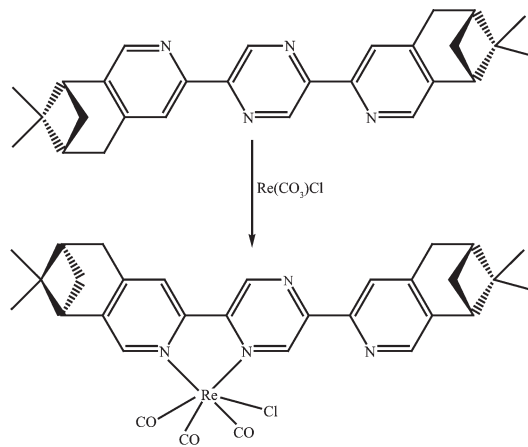


Scheme 1 Synthetic route of the Re(I) complex

# 1 Experimental

## 1.1 General

Organic reagents and Re(CO)$_3$Cl were purchased from Sigma-Aldrich and used as received. Elemental analysis for C, H and N were performed on a Perkin-Elmer 240C analyzer. Solid infrared spectra were recorded on a Vector22 Bruker Spectrophotometer with KBr pellets in the 400~4 000 cm$^{-1}$ region. UV-Vis absorption spectra were recorded on Shimadzu

UV-2700 Spectrophotometer using dichloromethane solutions. Luminescence spectra were recorded in dichloromethane solution on HITACHI F-4600 Fluorescence Spectrophotometer.

## 1.2　Synthesis

The ligand 2,5-bis(4,5-pinene-2-pyridyl) pyrazine was prepared according to the literature method [12], and red crystals suitable for X-ray structure analysis were obtained by the recrystallization in acetonitrile and dimethylformamide. IR　(KBr) / cm$^{-1}$: 3 432 (m), 2 929 (s),1 600 (m), 1 556 (m), 1 466 (s), 1 426 (m), 1 385 (m), 1 325 (m), 1 255 (m), 1 168 (m), 1 068 (m), 1 020 (m), 947 (m), 910 (m), 880 (m).

The rhenium(I) complex was prepared by addition of the ligand 2,5-bis(4,5-pinene-2-pyridyl) pyrazine to [Re(CO)$_3$Cl] in a 1.5:1 molar ratio in methanol under reflux conditions for 12 h. Following removal of the solvent in vacuo, the residue was extracted with dichloromethane and purified by chromatography (silica gel, ethyl acrylate-dichloromethane 1:1). Orange rod-shaped crystals suitable for X-ray structure analysis were obtained by evaporation of a concentrated solution of the complex in dichloromethane and dimethylformamide. Anal. calcd for C$_{34}$H$_{37}$N$_5$O$_4$ClRe(%): C, 50.96; H, 4.65; N, 8.74. Found (%): C, 51.01; H, 4.77; N, 8.69. IR (KBr)/cm$^{-1}$: 3 447 (m), 2 933 (m), 2 020 (s), 1 918 (s), 1 895 (s), 1 468 (m), 1 177 (m).

## 1.3　X-ray crystallography

The crystal structures of the ligand 2,5-bis(4,5-pinene-2-pyridyl) pyrazine and Re(I) complex have been solved by X-ray diffraction analysis. Their main crystallographic data are summarized in Table 1.

**Table 1　Crystallographic data for the ligand and Re(I) complex**

| | | |
|---|---|---|
| Empirical formula | C$_{34}$H$_{37}$ClN$_5$O$_4$Re | C$_{28}$H$_{30}$N$_4$ |
| Formula weight | 801.34 | 422.56 |
| Temperature / K | 296(2) | 296(2) |
| Wavelength / nm | 0.071 073 | 0.071 073 |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | $P2_12_12_1$ | $P2_1$ |
| $a$ / nm | 1.273 61(5) | 0.713 7(7) |
| $b$ / nm | 1.457 54(6) | 0.896 58(6) |
| $c$ / nm | 1.852 74(7) | 1.918 1(8) |
| $\beta$ / (°) | | 91.441(16) |
| Volume / nm$^3$ | 3.439 3(2) | 1.227 0(13) |
| $Z$ | 4 | 2 |
| $D_c$ / (g·cm$^{-3}$) | 1.548 | 1.144 |
| Absorption coefficient / mm$^{-1}$ | 3.654 | 0.068 |
| $F(000)$ | 1 600 | |
| $\theta$ range for data collection / (°) | 1.78 to 26.00 | 1.06 to 26.00 |
| Index ranges | $-15 \leqslant h \leqslant 15$, $-17 \leqslant k \leqslant 17$, $-19 \leqslant l \leqslant 22$ | $-8 \leqslant h \leqslant 8$, $-11 \leqslant k \leqslant 11$, $-23 \leqslant l \leqslant 23$ |
| Reflections collected | 20 982 | 9 905 |
| Independent reflections | 6 748 ($R_{int}$=0.027 8) | 4 798 ($R_{int}$=0.026 3) |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max. and min. transmission | 0.696 and 0.522 | 0.987 8 and 0.981 1 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 6 748 / 7 / 412 | 4 798 / 1 / 293 |
| Goodness-of-fit on $F^2$ | 1.038 | 1.027 |
| Final $R$ indices ($I>2\sigma(I)$) | $R_1$=0.028 7, $wR_2$=0.070 5 | $R_1$=0.053 1, $wR_2$=0.117 4 |
| $R$ indices (all data) | $R_1$=0.031 9, $wR_2$=0.071 5 | $R_1$=0.069 8, $wR_2$=0.119 2 |
| Absolute structure parameter | 0.014(8) | −10(4) |
| Largest diff. peak and hole / (e·nm$^{-3}$) | 943 and −668 | 180 and −171 |

Intensity data were collected on a Bruker SMART CCD diffractometer using monochromated Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm) at room temperature. The collected frames were processed with the software SAINT[21]. The structures were solved by the direct method and refined by full-matrix least-squares on $F^2$ using the program SHELXTL-97[22]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated position or found in the difference Fourier maps. The ligand contains only light scattering atoms (C, H and N), and the anomalous scattering is not obvious whether using Cu or Mo target, so the absolute structure of it can not be determined reliably and the Flack parameter is meaningless.

CCDC: 921976, complex; 921977, ligand.

## 1.4 CD and VCD spectra measurements

CD spectra were recorded on a Jasco J-810 spectropolarimeter by using 1 cm quartz cell. Conditions of measurements included a scanning speed of 200 nm·min⁻¹, a step size of 0.5 nm, a bandwidth of 2 nm, a response time of 0.5 s, standard sensitivity setting, and an accumulation of 5 scans at room temperature. The baseline was corrected by subtracting the signal of blank solution (dichloromethane) under the same condition. The solution IR and VCD spectra were recorded on a VERTEX 80v Fourier transform infrared spectrometer equipped with a PMA 50 VCD/IRRAS module (Bruker, Germany) in the region of 1 800~800 cm⁻¹ [23-24]. The photo elastic modulator (PEM) was set to 1 500 cm⁻¹, the spectral resolution was 4 cm⁻¹, and the zero filling factor was 4. For each set of measurements, a multiple-wave plate (CdS) combined with the second wire grid linear polarizer was employed to calibrate the phase of the

lock-in amplifier. A demountable cuvette A145 with BaF₂ with 0.10 mm Teflon spacer was used. All solution samples were dissolved in deuterated chloroform (CDCl₃). The concentration of the ligand was 0.35 mol·L⁻¹, while the concentration of the complex was 0.25 mol·L⁻¹. All VCD measurements were collected for 4 h composed of 12 blocks, each consisting of 1420 scans accumulated for 20 min. Baseline correction was performed with the spectra of deuterated solvent using the same measurement setup as for VCD.

## 1.5 Measurement of SHG responses

Powders of samples were graded by using standard sieves to particle sizes with diameters of 80~ 150 μm (checked by standard optical microscopy technique) and were placed on a microscope slide and held in place with transparent tape. The second-order NLO intensities were estimated by the method previously reported by Kurtz and Perry[25], with the use of a pulsed Q-switched Nd:YAG laser ($\lambda$=1 064 nm) to generate the SHG signal. The backward scattered SHG light was collected by employing a spherical concave mirror and passed through a filter that transmits only 532-nm radiation. The SHG efficiencies of the samples were estimated by comparison with that obtained for urea.

## 2 Results and discussion

### 2.1 X-ray structure

Fig.1 shows the crystal structure of the ligand 2,5-bis (4,5-pinene-2-pyridyl) pyrazine. Selected bond lengths and angles are listed in Table 2. The nitrogen atoms are distributed alternatively on the two side of the molecular axis. The pyridine rings on both ends are non-coplanar to the central pyrazine ring (Fig.1), with the dihedral angles of 21.709° and 10.209°,
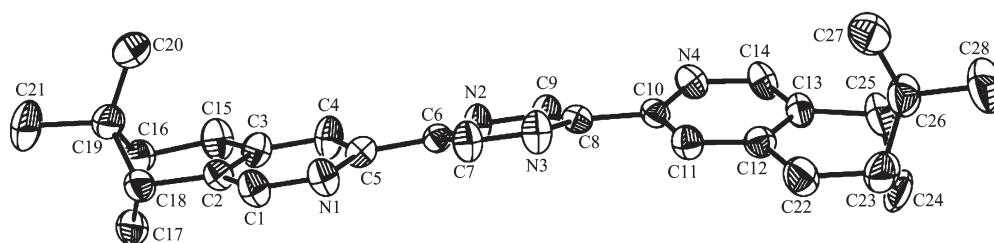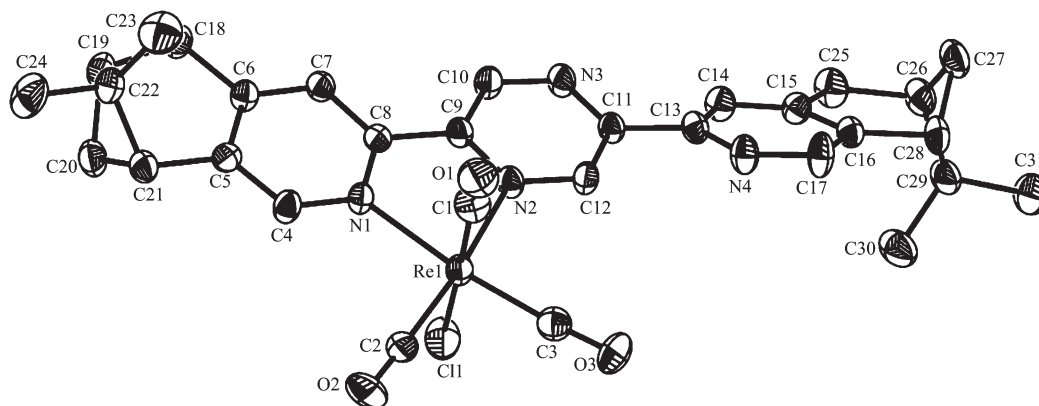


H atoms are omitted for clarity

Fig.1 X-ray structure of the ligand

**Table 2　Select bond lengths (nm) and angles (°) for the ligand and complex**

| Ligand | | | | | |
|---|---|---|---|---|---|
| C1-N1 | 0.133 4(4) | C4-N1 | 0.133 5(4) | C10-N4 | 0.135 2(4) |
| C2-N2 | 0.134 9(4) | C5-N3 | 0.135 8(4) | C11-N4 | 0.135 0(4) |
| C3-N2 | 0.133 9(4) | C9-N3 | 0.134 0(4) | | |
| | | | | | |
| C1-N1-C4 | 117.0(3) | C1-C2-C10 | 122.2(3) | N3-C5-C4 | 117.0(3) |
| C3-N2-C2 | 115.8(3) | N1-C4-C3 | 119.8(3) | C6-C5-C4 | 121.4(3) |
| C9-N3-C5 | 117.3(3) | N1-C4-C5 | 117.9(3) | N4-C10-C14 | 123.4(3) |
| C11-N4-C10 | 116.0(3) | C3-C4-C5 | 122.3(3) | N4-C10-C2 | 115.8(3) |
| N2-C2-C1 | 120.0(3) | N3-C5-C6 | 121.6(3) | C14-C10-C2 | 120.7(3) |
| N2-C2-C10 | 117.8(3) | | | | |
| Complex | | | | | |
| Re1-N1 | 0.217 5(4) | Re1-C2 | 0.192 8(6) | C1-O1 | 0.105 3(8) |
| Re1-N2 | 0.216 0(4) | Re1-C3 | 0.191 6(6) | O2-C2 | 0.113 5(6) |
| Re1-C1 | 0.197 9(7) | Re1-Cl1 | 0.242 07(19) | O3-C3 | 0.116 7(7) |
| | | | | | |
| C3-Re1-C2 | 88.9(2) | C1-Re1-N2 | 92.4(2) | C3-Re1-Cl1 | 94.0(2) |
| C3-Re1-C1 | 89.4(3) | C3-Re1-N1 | 173.1(2) | C2-Re1-Cl1 | 93.58(18) |
| C2-Re1-C1 | 91.2(3) | C2-Re1-N1 | 98.05(19) | C1-Re1-Cl1 | 174.22(18) |
| C3-Re1-N2 | 97.5(2) | C1-Re1-N1 | 90.0(2) | N2-Re1-Cl1 | 82.55(13) |
| C2-Re1-N2 | 172.7(2) | N2-Re1-N1 | 75.59(15) | N1-Re1-Cl1 | 86.09(12) |



H atoms and solvent DMF molecule are omitted for clarity

Fig.2　X-ray structure of Re(CO)$_3$Cl(L)·DMF

respectively.

Fig.2 shows the crystal structure of the Re(I) complex. The asymmetric unit consists of a [Re(CO)$_3$Cl(L)] complex and a free solvent DMF molecule. The 4,5-pinene-2-pyridine turns around the C-C bond, thus providing two ipsi-lateral nitrogen atoms to bind the Re(I) center. The 2,5-bis (2-pyridyl) pyrazine moiety is less distorted from co-planarity (the dihedral angles of the pyridine ring to the pyrazine ring are 23.700° and 6.267°, respectively). Due to the turnover of the 4,5-pinene-2-pyridine groups, the coplanarity (vide infra) further decreases. The Re(I) is surrounded by an approximated octahedral arrange-ment of two nitrogen atoms (N1, N2) from the chiral ligand, three carbon atoms (C1, C2 and C3) from CO, and one chlorine atom (Cl1). The mean Re-N and Re-C bond lengths are 0.216 8 and 0.194 1 nm respectively, and the Re-Cl bond length is larger with the value 0.242 07 nm (Table 2). The three CO ligands are in end-on coordination, and they are in close proximity with the

ligand backbone.

## 2.2 Absorption and emission spectra

Fig.3 presents the absorption spectra of the ligand and Re (I) complex in dichloromethane solutions with a concentration of $1 \times 10^{-5}$ mol·L$^{-1}$. Absorption spectra of the ligand and Re(I) complex are very similar. The ligand shows lower intensity UV band with three peaks at 225, 264 and 333 nm, which can be attributed to $\pi \rightarrow \pi^*$ interligand transitions (K band)[26]. In the Re(I) complex, the bands exhibit red shift to 255, 307 and 376 nm. The moderately intense, poorly distinguished absorption band extending into the visible region from *ca.* 400 to 600 nm was tentatively assigned to an admixture of metal-to-ligand charge transfer states $d\pi(Re) \rightarrow \pi^*(L)$.
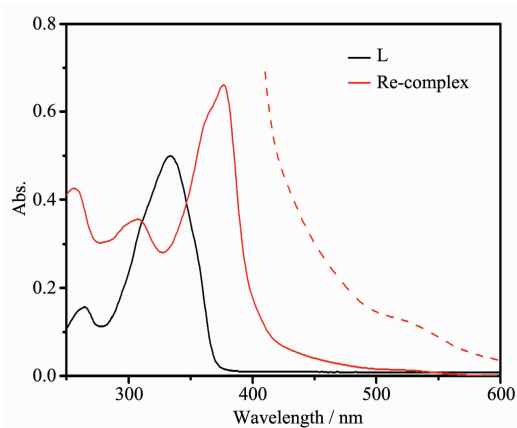


Consentration: ligand $c = 10^{-5}$ mol·L$^{-1}$; complex $c = 10^{-5}$ mol·L$^{-1}$ (solid line) and $10^{-3}$ mol·L$^{-1}$ (dash line)] in CH$_2$Cl$_2$ solutions

Fig.3　Absorption spectra of the ligand and Re(I) complex

When excited in dichloromethane solution at room temperature within maximum excitation wavelength, the ligand and Re (I) complex exhibit maximum emission at 420 and 650 nm, respectively (Fig.4). The full width at half maximum (FWHM) of the emission spectrum of Re(I) complex is ~120 nm, which is typical for MLCT-based luminescence in this type of complex[27-28]. There is little overlap between the absorption and emission spectra of the Re (I) complex. The Stokes shift is as large as about 270 nm, which should be caused by significant structural differences between the ground state and excited state upon photo excitation[29]. In the experiment, we also

observed that the kind of solvents can influence the fluorescence, when using polarity stronger acetonitrile or methanol as solvents will induce fluorescent quenching.
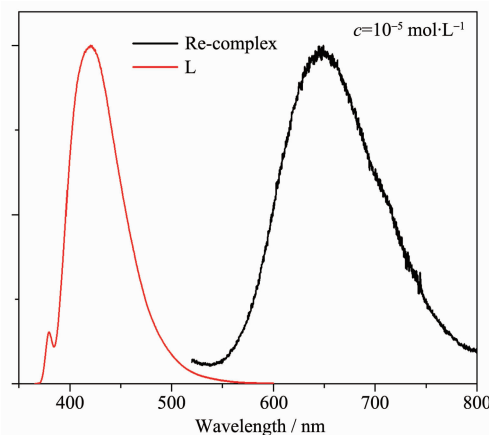


Fig.4　Emission spectra of the ligand and Re(I) complex in CH$_2$Cl$_2$ solutions

## 2.3 ECD and VCD spectra

Fig.5 presents the ECD spectra of the ligand and Re(I) complex in dichloromethane solutions with a concentration of $5 \times 10^{-5}$ mol·L$^{-1}$. The ECD spectrum of the ligand shows a vibronic negative Cotton effects at 331 nm with a shoulder at 276 nm. The Re(I) complex exhibits three negative Cotton effects at 263, 302, and 375 nm, respectively. All these features are in good agreement with the UV-Vis spectra.
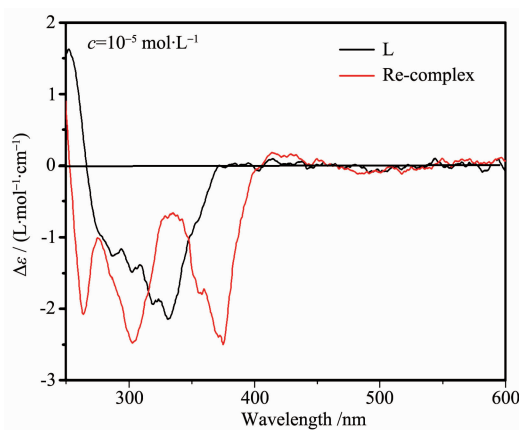


Fig.5　ECD spectra of the ligand and Re(I) complex in CH$_2$Cl$_2$ solutions

The IR and VCD spectra of the ligand and Re(I) complex in CDCl$_3$ solutions are shown in Fig.6. The IR spectrum of the Re(I) complex is similar to that of the bare ligand, in spite that some of the vibration

energies are shifted due to coordination. Distinct bisignate signals at 1 450~1 490 cm⁻¹, corresponding to the most prominent peaks　(1 461 cm⁻¹ for the ligand and 1 468 cm⁻¹ for the Re(I) complex) in the IR spectra, were observed in the VCD spectra. These signals can be ascribed to the vibration of C-H bond in the pinene groups. Interestingly, the intensity of the bisignate signals are significantly enhanced in the Re(I) complex. This is in agreement with the X-ray crystallographic results that the ligand forms single-helical structure in the Re(I) complex.
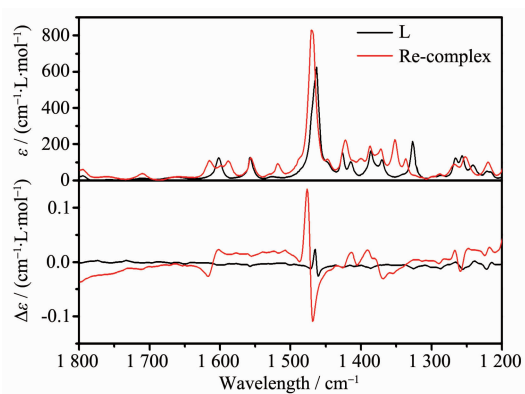


Fig.6　IR and VCD spectra of the ligand and Re(I) complex in CDCl₃ solutions

### 2.4　Second-order NLO properties

Both the ligand and Re(I) complex show second-order NLO properties. The second harmonic generation (SHG) responses of the ligand and Re(I) complex estimated using the Kurtz powder method[25] according to the literature procedure are ~0.4 and ~0.3 times that of urea, respectively. The SHG response of the ligand is higher than that of the Re(I) complex, in spite that the chirality is increased in the Re(I) complex as revealed by X-ray crystallography and VCD spectroscopic study. This is due to that the ligand crystallizes in the polar $P2_1$ space group. However, the Re(I) complex crystallizes in the non-polar $P2_12_12_1$ space group. The three orthogonal twofold screw axes in $P2_12_12_1$ space group will cancel the molecular dipoles and collectively reduce the net dipole moment and hyperpolarizability[30].

## 3　Conclusions

In this paper, a chiral ligand 2,5-bis(4,5-pinene-2-pyridyl) pyrazine　(L) and its rhenium(I) complex [Re(CO)₃Cl(L)]·DMF were synthesized and characterized. Both ligand and [Re(CO)₃Cl(L)]·DMF show optical activity as manifested by the ECD and VCD spectra. Upon excitation, the ligand and Re(I) complex emit at 420 nm and 650 nm, respectively. X-ray crystallographic analysis shows that the ligand crystallizes in monoclinic $P2_1$ space group while [Re(CO)₃Cl(L)]·DMF crystallizes in orthorhombic $P2_12_12_1$ space group. Both the ligand and Re(I) complex show second-order non-linear optic　(NLO) properties as they crystallize in non-centric space groups.

### References:

[1] Amouri H, Gruselle M. *Chirality in Transition Metal Chemistry*: *Molecules, Supramolecular Assemblies and Materials*. Chichester: John Wiley & Sons, **2008**.

[2] von Zelewsky A. *Stereochemistry of Coordination Compounds*. Chichester: John Wiley & Sons, **1996**.

[3] Liu J, Zhang X P, Wu T, et al. *Inorg. Chem.*, **2012**,**51**:8649-8651

[4] Zhang J, Gao S, Zhang X X, et al. *Dalton Trans.*, **2012**,**41**: 2626-2631

[5] Mutti F G, Zoppellaro G, Gullotti M, et al. *Eur. J. Inorg. Chem.*, **2009**,**4**:554-566

[6] Mejia E, Aardoom R, Togni A. *Eur. J. Inorg. Chem.*, **2012**, **31**:5021-5032

[7] Chen Q, Zhou J, Han Q, et al. *J. Solid State Electrochem.*, **2012**,**16**:2481-2485

[8] Gong L, Mulcahy S P, Harms K, et al. *J. Am. Chem. Soc.*, **2009**,**131**:9602-9603

[9] Pradeep C P, Zacharias P S, Das S K. *Eur. J. Inorg. Chem.*, **2007**,**34**:5377-5389

[10]Hamann C, von Zelewsky A, Neels A, et al. *Dalton Trans.*, **2004**,**3**:402-406

[11]Knof U, von Zelewsky A. *Angew. Chem. Int. Ed.*, **1999**,**38**: 302-322

[12]Bark T, Stoeckli-Evans H, von Zelewsky A. *J. Chem. Soc. Perkin Trans.*, **2002**,**16**:1881-1886

[13]Malkov A V, Stewart-Liddon A J P, Teply F, et al. *Tetrahedron*, **2008**,**64**:4011-4025

[14]Malkov A V, Bella M, Langer V, et al. *Org. Lett.*, **2000**,**2**: 3047-3049

[15]Rich J, Rodriguez M, Romero I, et al. *Dalton Trans.*, **2009**, **38**:8117-8126

[16]Mamula O, Lama M, Telfer S G, et al. *Angew. Chem. Int. Ed.*, **2005**,**44**:2527-2531

[17]Yi X Y, Zhao J Z, Wu W H, et al. *Dalton Trans.*, **2012**,**41**: 8931-8940

[18]Oriskovich T A, White P S, Thorp H H. *Inorg. Chem.*, **1995**, **34**:1629-1631

[19]Esteves T, Xavier C, Gama S, et al. *Org. Biomol. Chem.*, **2010**,**8**:4104-4116

[20]Yeung H L, Wong W Y, Wong C Y, et al. *Inorg. Chem.*, **2009**,**48**:4108-4117

[21]*SAINT, Area Detector Control and Integration Software*, Siemens Analytiacl X-ray instruments Inc., Madison, WI, USA, **1996**.

[22]Sheldrick G M. *SHELXTL*-97, *Program for Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[23]Wu T, Li C H, Li Y Z, et al. *Dalton Trans.*, **2010**,**39**:3227-3232

[24]Wu T, Zhang X P, Li C H, et al. *Chirality*, **2012**,**24**:451-458

[25]Kurtz S K, Perry T T. *J. Appl. Phys.*, **1968**,**39**:3798-3813

[26]Lama M, Mamula O, Kottas G S, et al. *Inorg. Chem.*, **2008**, **47**:8000-8015

[27]Uddin M J, Dicesare N, Lakowicz J R. *Inorg. Chim. Acta*, **2012**,**381**:104-110

[28]Waterland M R, Simpson T J, Gordon K C, et al. *J. Chem. Soc., Dalton Trans.*, **1998**,**1**:185-192

[29]Li X, Zhang D Y, Lu G H, et al. *J. Photochem. Photobio. A*, **2012**,**214**:1-7

[30]Li D P, Li C H, Wang J, et al. *Eur. J. Inorg. Chem.*, **2009**, **32**:4844-4849