

两个手性 Salen 型过渡金属配合物的合成、波谱与结构

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摘要: 本文报道了 2 个手性 Salen 型过渡金属配合物[(*N,N'*-bis(3-*t*-butyl-5-methylsalicylidene)-1*S*,2*S*-cyclohexanediamine-*N,N',O,O'*) nickel(II)] (**1**)和[(*N,N'*-bis(3-*t*-butyl-5-methylsalicylidene)-1*S*,2*S*-cyclohexanediamine-*N,N',O,O'*) copper(II)] (**2**)的合成、波谱与结构表征。它们由(1*S*,2*S*)-环己烷-1,2-二胺和 3-叔丁基-5-甲基-2-羟基苯甲醛发生席夫碱缩合反应制得的配体分别与 Cu(II)和 Ni(II)盐反应而得到。产品经过红外光谱、元素分析、电喷雾质谱、紫外和圆二色光谱等方法表征,并测定其晶体结构。结果表明配合物 **1** 和 **2** 中的中心金属离子 Cu(II)和 Ni(II)均为四配位平面正方形配位构型, 而且在其晶体堆积中观察到一种通过芳环之间弱 π - π 相互作用形成的二聚结构。

关键词: Salen 型配合物; 席夫碱缩合反应; 晶体结构; 圆二色性

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Syntheses, Spectral and X-ray Crystal Structural Studies of Two Chiral Salen-Type Transition-Metal Complexes

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Abstract: Two chiral Salen-type transition-metal complexes, named as (*N,N'*-bis(3-*t*-butyl-5-methylsalicylidene)-1*S*,2*S*-cyclohexanediamine-*N,N',O,O'*) nickel(II) (**1**) and (*N,N'*-bis(3-*t*-butyl-5-methylsalicylidene)-1*S*,2*S*-cyclohexanediamine-*N,N',O,O'*) copper(II) (**2**), were obtained from the Schiff base condensation between (1*S*,2*S*)-cyclohexane-1,2-diamine and 3-*tert*-butyl-5-methyl-2-hydroxybenzaldehyde. X-ray diffraction crystal structural analyses of **1** and **2** demonstrate that they are isostructural and each central metal ion (M(II)) presents square-planar coordination configuration. Both of them are fully characterized by mass spectrometry, FTIR, elemental analysis, UV-Vis spectra and circular dichroism (CD) spectra. A dimeric packing mode via weak offset π - π stacking is observed in the crystal packing structures of **1** and **2**. CCDC: 685302, **1**; 685303, **2**.

Key words: Salen-type complex; Schiff base condensation; crystal structure; circular dichroism

Salen-type ligands derived from salicylaldehydes and diamines are amongst the oldest ligands in

coordination chemistry and have received considerable interest since Jacobsen and Katsuki first reported their

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significant success using chiral manganese(III) Salen-type Schiff base catalysts in the asymmetric epoxidation of unfunctionalised olefins^[1,2]. Over the past decade, many metal-Salen complexes have been synthesized and found to be active in asymmetric catalysis because subtle change of the substituted groups at 3 and 5 positions of 2-hydroxybenzaldehyde (H, H; H, CH₃; CH₃, CH₃; CH₃, *t*-Bu; *t*-Bu, *t*-Bu) and the type of metal ions will influent greatly the activation of the resulting Salen-type complexes^[3,4]. For example, they can be used for enantioselective cyclopropanation of styrenes^[5], asymmetric aziridination of olefins^[6], asymmetric Diels-Alder cycloaddition reactions^[7], asymmetric epoxide ring-opening reactions^[8], and chemical sensors^[9]. Many of these complexes have been successfully characterized by X-ray crystal structure determination. In all of these complexes the dianionic *N,N',O,O'*-tetradentate binding mode is observed. In addition, some of these complexes contain axial ligands in some cases, both neutral and anionic, depending on the charge and the coordination geometry of the central metal ions.

In our systematic work on Schiff base macrocyclic complexes prepared from the sodium (I) template condensation^[10,11], many compartmental macrocyclic mono or polynuclear transition-metal complexes have been obtained including several chiral Salen-type transition-metal complexes^[12]. In this paper, we report the syntheses, crystal structures and spectroscopic characterizations of one Cu(II) and one Ni(II) complexes (**1**) and (**2**) obtained from the metal ion complexation after the Schiff base condensation between (1*S*,2*S*)-cyclohexane-1,2-diamine and 3-*tert*-butyl-5-methyl-2-hydroxybenzaldehyde.

1 Experimental section

1.1 Materials and measurements

Chiral (1*S*,2*S*)-cyclohexane-1,2-diamine was purchased directly from Aldrich. 3-*t*-Butyl-5-methyl-2-hydroxybenzaldehyde was prepared as reported previously^[13]. Schiff base ligand (*S,S*-*L*) was prepared from (1*S*,2*S*)-cyclohexane-1,2-diamine and 3-*t*-butyl-5-methyl-2-hydroxybenzaldehyde by a standard Schiff

base condensation. The other reagents were of analytical grade from commercial sources and were used without any further purification.

Elemental analyses were measured with a Perkin-Elmer 1400C analyzer. Infrared spectra (4 000~400 cm⁻¹) were collected on a Nicolet FTIR 170X spectrophotometer at 25 °C using KBr plates. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan MAT SSQ 710 mass spectrometer in a scan range 100~1 200 amu. The UV-Vis spectra were recorded on a Shimadzu UV-3100 double-beam spectrometer using a Pyrex cell with a path length of 10 mm at room temperature. The circular dichroism (CD) spectra were measured with a JASCO J-810 spectropolarimeter using the same solutions as those for the UV-Vis determination.

1.2 Preparation of complexes **1** and **2**

Complex **1** (*N,N'*-bis(3-*t*-butyl-5-methylsalicylidene)-1*S*,2*S*-cyclohexanediamine-*N,N',O,O'*) nickel(II): A solution of Ni(OAc)₂·4H₂O (0.075 g, 0.3 mmol) in 10 mL methanol was dropped into a solution of the chiral ligand (*S,S*-*L*) (0.138 g, 0.3 mmol) in 10 mL of methanol. The reaction was refluxed for 2 h, resulting in a brown precipitate. The precipitate was filtered, washed with a small amount of ethanol and dried in a vacuum. Yields: 85% (0.132 g). FTIR (KBr, cm⁻¹): 3 423(m), 2 946(s), 2 862(m), 1 615(C=N, s), 1 535(s), 1 455(w), 1 433(s), 1 385(m), 1 341(m), 1 318(s), 1 171(m), and 820 (w). ESI-MS: 541.6 (1+Na⁺, 100%), 519.6 (62%). Anal. Calcd. for C₃₀H₄₀NiN₂O₂ (%): C, 69.38; H, 7.76; N, 5.39. Found (%): C, 69.33; H, 7.71; N, 5.37. Single-crystal samples of **1** suitable for X-ray diffraction were grown from the mixed solution of CH₃CN/CH₃CH₂OH (*V/V*=1:2) by slow evaporation in air at room temperature.

Complex **2** (*N,N'*-bis(3-*t*-butyl-5-methylsalicylidene)-1*S*,2*S*-cyclohexanediamine-*N,N',O,O'*) copper(II) was obtained as green solid by the similar procedure to that of complex **1** using Cu(OAc)₂·3H₂O (0.071 g, 0.3 mmol) instead of Ni(OAc)₂·4H₂O to react with the chiral ligand (*S,S*-*L*). Yields: 83% (0.131 g). FTIR (KBr, cm⁻¹): 3 423(m), 2 944(m), 2 861(m), 1 617(C=N, s), 1 532(s),

1 462(w), 1 428(s), 1 383(m), 1 344(m), 1 319(s), 1 166(m), and 815(w). ESI-MS: 546.5 (2+Na⁺, 100%), 524.6 (78%). Anal. Calcd. for C₃₀H₄₀CuN₂O₂ (%): C, 68.74; H, 7.69; N, 5.34. Found (%): C, 68.72; H, 7.76; N, 5.29. Single-crystal samples of **2** suitable for X-ray diffraction were grown from the mixed solution of CH₃CN/CH₃OH (V/V=1:1) by slow evaporation in air at room temperature.

1.3 X-ray crystal structure analyses

Single-crystal X-ray diffraction data of **1** and **2** were measured on a Siemens SMART CCD diffractometer using graphite-monochromatized Mo K α radiation (λ =0.071 073 nm). Data collection was performed by using SMART program^[14]. Cell refinement and data reduction were made with the SAINT program^[15]. The structures were solved by directed method and refined

on F^2 by using full-matrix least-squares methods with SHELXTL version 6.10^[16]. All non-hydrogen atoms were refined by using anisotropic displacement parameters. Hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. For complexes **1** and **2**, the absolute configuration of chiral carbon atoms cannot be specified because the carbon atoms C13, C14 and C17 of cyclohexane-1,2-diamine moieties in the ligand are found disordered at two positions with equal site occupancy factors. The summary of the crystal data, experimental details and refinement results for **1** and **2** is listed in Table 1, while selected bond distances and bond angles are given in Table 2.

CCDC: 685302, **1**; 685303, **2**.

Table 1 Crystal and structure refinement data for **1** and **2**

Compound	1	2
Empirical formula	C ₃₀ H ₄₀ NiN ₂ O ₂	C ₃₀ H ₄₀ CuN ₂ O ₂
Formula weight	519.33	524.19
Crystal size / mm	0.10×0.20×0.20	0.10×0.10×0.20
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	0.867 5(1)	0.877 4(1)
b / nm	1.273 0(1)	1.268 5(1)
c / nm	1.356 6(1)	1.366 4(1)
α / (°)	106.38(1)	107.117(2)
β / (°)	104.62(1)	105.35(1)
γ / (°)	94.75(1)	93.74(1)
V / nm ³	1.3715(3)	1.3846(3)
Z	2	2
D_c / (Mg·m ⁻³)	1.258	1.257
$F(000)$	556	558
μ / mm ⁻¹	0.736	0.817
h_{\min} / h_{\max}	-10 / 10	-10 / 10
k_{\min} / k_{\max}	-15 / 14	-14 / 15
l_{\min} / l_{\max}	-10 / 16	-15 / 16
Refl. total	6 912	7 358
Refl. collected / unique	4 758 / 4 227 (R_{int} =0.042 9)	5 076 / 2 500 (R_{int} =0.047 5)
Parameters	351	339
Max. / min. transmissions	0.930 1 / 0.866 8	0.922 8 / 0.853 7
Final R indices [$I > 2\sigma(I)$]	R_1 =0.048 7, wR_2 =0.123 8	R_1 =0.053 8, wR_2 =0.089 1
R indices (all data)	R_1 =0.054 4, wR_2 =0.126 4	R_1 =0.114 0, wR_2 =0.099 2
Goodness-of-fit on F^2	1.012	0.915
Max. / min., $\Delta\rho$ / (e·nm ⁻³)	410 / -320	260 / -250

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) for **1** and **2**

1		2	
Ni(1)-O(1)	0.184 1(2)	Cu(1)-O(1)	0.187 8(3)
Ni(1)-O(2)	0.184 9(2)	Cu(1)-O(2)	0.189 1(3)
Ni(1)-N(1)	0.184 1(3)	Cu(1)-N(1)	0.192 5(3)
Ni(1)-N(2)	0.185 1(3)	Cu(1)-N(2)	0.193 3(4)
O(1)-Ni(1)-O(2)	85.79(10)	O(1)-Cu(1)-O(2)	90.45(12)
O(1)-Ni(1)-N(1)	94.37(11)	O(1)-Cu(1)-N(1)	93.25(14)
O(1)-Ni(1)-N(2)	174.91(13)	O(1)-Cu(1)-N(2)	171.27(14)
O(2)-Ni(1)-N(1)	174.67(13)	O(2)-Cu(1)-N(1)	171.33(15)
O(2)-Ni(1)-N(2)	94.34(11)	O(2)-Cu(1)-N(2)	93.12(14)
N(1)-Ni(1)-N(2)	85.97(13)	N(1)-Cu(1)-N(2)	84.34(16)

2 Results and discussion

2.1 Spectral characterization

The FTIR spectra of **1** and **2** display sharp peaks characteristic of the C=N double bond at 1 615 and 1 617 cm^{-1} , respectively. Positive ESI-MS spectra in ethanol solutions of **1** and **2** show predominant peaks centered at $m/z=541.6$ and 546.5, respectively, which are in good agreement with the presence of [**1** or **2**+Na] $^{+}$ cations.

The UV-Vis spectra of **1** and **2** are slightly different due to their different d^8 (Ni^{2+}) and d^9 (Cu^{2+}) configuration (Fig.1). Complex **1** presents three UV-Vis absorption bands at 275, 346 and 421 nm and three corresponding cotton peaks (the inset of Fig.1) by contrast: 263 (+), 350 (+) and 415 (+) nm. Compared with the Ni(II) complex **1**, **2** exhibits three absorption bands at 247, 279 and 376 nm in the UV-Vis

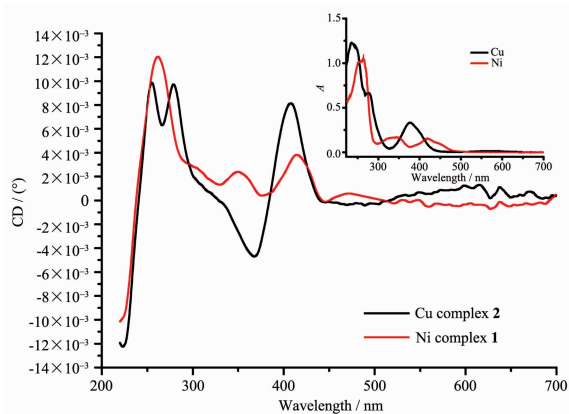


Fig.1 UV-Vis and CD absorption spectra of **1** and **2** in ethanol

absorption spectrum. The intense bands at 247 and 279 nm originate from the $\pi-\pi^*$ transition of the benzene ring of salicylaldehyde, whilst the moderate absorption band near 376 nm is assigned to the $\pi-\pi^*$ transition of the azomethine chromophore.

However, the CD spectrum of **2** shows four cotton peaks at 252 (+), 281 (+), 368 (-) and 403 (-) nm by contrast. The UV-Vis absorption bands at 247 and 279 nm are corresponding with the CD bands at 252(+) and 281(+) and the absorption band at 376 nm is corresponding with the CD bands splitting into 368(-) and 403(+) nm. The sign patterns of the CD spectra of complexes **1** and **2** (positive cotton effects) suggest the intrinsic chiral nature of the (1*S*,2*S*)-cyclohexane-1,2-diamine because it is found that (1*S*,2*S*)-cyclohexane-1,2-diamine based compounds give positive cotton effects in their CD spectra.

2.2 Crystal structures of **1** and **2**

The single-crystal structures show that complex **1** is isomorphous with complex **2**. Due to the disorder of chiral carbon atoms, both complexes crystallize in the centrosymmetric space group $P\bar{1}$. As illustrated in Fig. 2, the metal centers are four-coordinated and the coordination geometry of center M(II) are square planar, with two imine N atoms N(1), N(2) and two phenolic O atoms O(1), O(2) occupying the equatorial positions. The bond lengths of Ni-O (0.184 1(2) and 0.184 1(2) nm) and Ni-N (0.184 9(3) and 0.185 1(3) nm) are shorter

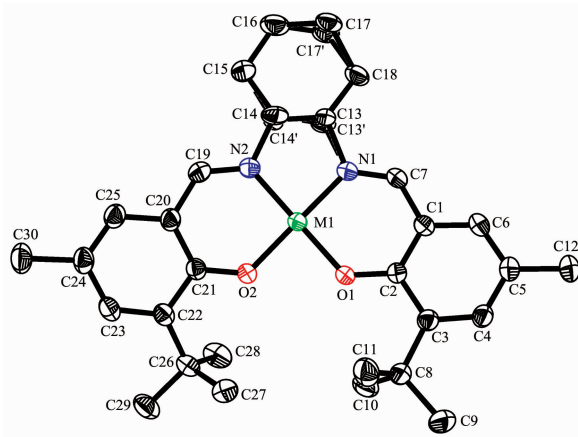
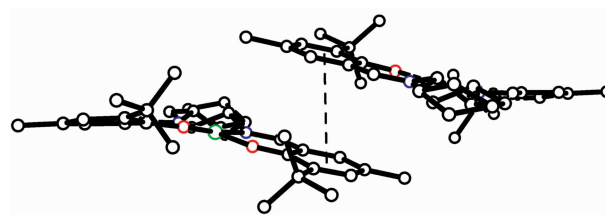


Fig.2 Molecular structures of **1** (M1=Ni(II)) and **2** (M1=Cu(II)) with the atom-numbering scheme (thermal ellipsoids at the 30% probability level); hydrogen atoms are omitted for clarity

than those of Cu-O (0.187 8(3) and 0.189 1(3) nm) and Cu-N (0.192 5(3) and 0.193 3(4) nm). The equatorial angles around the central M(II) centers are [N(1)-Ni(1)-N(2) 85.97(13)°, O(1)-Ni(1)-O(2) 85.79(10)°, O(1)-Ni(1)-N(1) 94.37(11)° and O(2)-Ni(1)-N(2) 94.34(11)°, N(1)-Cu(1)-N(2) 84.34(16)°, O(1)-Cu(1)-O(2) 90.45(12)°, O(1)-Cu(1)-N(1) 93.25(14)° and O(2)-Cu(1)-N(2) 93.12(14)°], which indicate that the M(II) ions deviate from the coordination planes to different extent. The mean deviations from least-squares plane are 0.006 74 nm in **1** and 0.010 84 nm in **2**, and the dihedral angles between the two aromatic rings within the molecules are 21.8° in **1** and 22.0° in **2**. The geometry of bond lengths and bond angles are comparable with those Salen-type complexes having four-coordinate metal centers but different substituted groups at 3 and 5 positions of 2-hydroxybenzaldehyde^[17-22].

In their crystal packing, all the molecules are essentially parallel and weak offset π - π stacking

interactions are observed between adjacent aromatic rings with the centroid-centroid separations of 0.400 3 nm in **1** and 0.404 1 nm in **2**, respectively (Fig.3). Thus, dimeric packing structures are formed in **1** and **2** where each Salen molecule points to the opposite direction. In addition, weak intramolecular C-H \cdots O hydrogen bonds are found between the hydrogen atoms of *t*-butyl groups and their neighboring phenoxy oxygen atoms with the average H \cdots O distance of 0.227 ~ 0.241 nm to further stabilize the Salen structures (Table 3).



Centroid-centroid separation is shown as the dotted line and the hydrogen atoms are omitted for clarity

Fig.3 A perspective view of the dimeric packing structures in **1** and **2**

Table 3 Intramolecular hydrogen-bond parameters in complexes **1** and **2**

D-H \cdots A	D-H / nm	H \cdots A / nm	D \cdots A / nm	\angle DHA / (°)
1				
C10-H10C \cdots O1	0.096	0.236	0.299 1(5)	123
C11-H11C \cdots O1	0.096	0.229	0.295 4(5)	126
C27-H27A \cdots O2	0.096	0.241	0.304 1(4)	123
C28-H28C \cdots O2	0.096	0.235	0.299 2(6)	124
2				
C10-H10C \cdots O1	0.096	0.235	0.299 3(5)	123
C11-H11C \cdots O1	0.096	0.227	0.293 0(5)	125
C27-H27A \cdots O2	0.096	0.236	0.300 4(5)	124
C28-H28C \cdots O2	0.096	0.234	0.297 5(5)	123

3 Conclusion

In summary, two new Ni(II) and Cu(II) complexes **1** and **2** with a Salen-type ligand derived from chiral (1*S*, 2*S*)-cyclohexane-1,2-diamine and 3-*t*-butyl-5-methyl-2-hydroxybenzaldehyde have been synthesized and characterized by EA, FTIR, ESI-MS, UV-Vis, CD and X-ray single-crystal structure analyses. Both complexes have four-coordinate square-planar metal centers and a dimeric packing mode via weak offset π - π stacking is observed in their crystal packing. In order to overcome the disorder of chiral cyclohexane-1,2-diamines in the

solid-state structures, the studies of preparing Schiff base metal complexes by using some other rigid or bulky chiral diamines are being undertaken.

References:

- [1] Zhang W, Loebach J L, Wilson S R, et al. *J. Am. Chem. Soc.*, **1990**,**11**(7):2801~2803
- [2] Irie R, Noda K, Ito Y, et al. *Tetrahedron Lett.*, **1990**,**31**(50): 7345~7348
- [3] Canali L, Sherrington D C. *Chem. Soc. Rev.*, **1999**,**28**(2):85~93
- [4] Cozzi P G. *Chem. Soc. Rev.*, **2004**,**33**(7):410~421
- [5] Niimi T, Uchida T, Irie R. *Tetrahedron Lett.*, **2000**,**41**(19):

- 3647~3651
- [6] Liang J L, Yu X Q, Che C M. *Chem. Commun.*, **2002**,**2**:124~125
- [7] Schaus S E, Branalt J, Jacobsen E N. *J. Org. Chem.*, **1998**,**63**(2):403~405
- [8] Jacobsen E N, Kakiuch F, Konsler R G, et al. *Tetrahedron Lett.*, **1997**,**38**(5):773~776
- [9] Libra E R, Scott M. *J. Chem. Commun.*, **2006**,**14**:1485~1487
- [10] Huang W, Zhu H B, Gou S H. *Coord. Chem. Rev.*, **2006**,**250**(3~4):414~423
- [11] Huang W, Chu Z L, Gou S H, et al. *Polyhedron*, **2007**,**26**(7):1483~1492
- [12] Chu Z L, Huang W, Wang L, et al. *Polyhedron*, **2008**,**27**(3):1079~1092
- [13] Larrow J F, Jacobsen E N. *J. Org. Chem.*, **1994**,**59**(7):1939~1942
- [14] Siemens, *SAINT V4 Software Reference Manual*, Siemens Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, **2000**.
- [15] Sheldrick G M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, Univ. of Gottingen, Germany, **2000**.
- [16] Siemens, *SHELXTL, Version 6.10 Software Reference Manual*, Siemens Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, **2000**.
- [17] Bunce S, Cross R J, Farrugia L J, et al. *Polyhedron*, **1998**,**17**:4179~4187
- [18] Bernardo K, Leppard S, Robert A, et al. *Inorg. Chem.*, **1996**,**35**(2):387~396
- [19] Szyk E, Barwioek M, Kruszynski R, et al. *Inorg. Chim. Acta*, **2005**,**358**(13):3642~3652
- [20] Sylvestre I, Wolowska J, Kilner C A, et al. *Dalton*, **2005**,**19**:3241~3249
- [21] Storr T, Wasinger E C, Pratt R C, et al. *Angew. Chem. Int. Ed.*, **2007**,**46**(27):5198~5201
- [22] Huang W, Chu Z L, Xu F. *J. Mol. Struct.*, **2008**,**885**:154~160