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C–H···Ni^{II} Interaction-Driven Homochiral *M* and *P* Helices of Neutral (*R*,*R*)- and (*S*,*S*)-Bis(pyrrol-2-ylmethyleneamino)cyclohexane Ni^{II} Complexes

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Reaction of (*R*,*R*)- and (*S*,*S*)-bis(pyrrol-2-ylmethyleneamino)cyclohexane with $Ni^{II}(OAc)_2{\cdot}4H_2O$ afforded enantiomeric nickel(II) Schiff-base complexes (*R*,*R*)-**1** and (*S*,*S*)-**1**, respectively. Rare C–H···Ni^{II} interactions were found to be responsible for the facile formation of homochiral *M* and *P* helices of the neutral, chiral, mononuclear complexes in crystal lattices.

Introduction

Inspired by biology and driven by applications in material science, chemists have made tremendous efforts in building helical arrays that play important roles across the whole spectrum of science and technology.[1–2] A large number of supramolecular helical architectures of coordination compounds have been constructed over the years.[2–6] It is known that the size and structure of the helix can be altered by subtle manipulation of the intermolecular interactions, such as hydrogen bonding, π–π stacking, and electrostatic and van der Waals forces.[1–6] Although C–H···M (M: metal) interaction was initially postulated in the literature,[7] its significance in self-assembling processes has not been realized until recently.[8] Ma and coworkers[8a] described in 2004 that the weak intermolecular C–H···Cu hydrogen bond plays a crucial role in constructing the network polymer of bis(pyrrol-2-ylmethyleneamine) ligands with Cu^{II}. Earlier work by Alyea et al.[8b] revealed that pairs of *cis*-$[PdCl_2(TPA)_2]$ (TPA = 1,3,5-triaza-7-phosphaadamantane) molecules are linked about inversion centers by intermolecular C–H···Pd hydrogen interactions, where water molecules link these dimers via O–H···N hydrogen bonds to form infinite chains that extends in the *c* direction in the crystal lattice.

In this communication, we report homochiral supramolecular left-handed (*M*) and right-handed (*P*) helices, which are derived from chiral neutral mononuclear (*R*,*R*)- and (*S*,*S*)-bis(pyrrol-2-ylmethyleneamino)cyclohexane nickel(II) complexes, (*R*,*R*)-**1** and (*S*,*S*)-**1**, respectively. The use of pyrrol-2-yl Schiff base avoids counterion coordination,[3c,8a] and thereby achieves exclusive coordination of the tetradentate ligand to nickel(II) center. X-ray crystal structural analysis reveals that (*R*,*R*)-**1** and (*S*,*S*)-**1** self-assemble via the intermolecular C–H···Ni^{II} interaction and the chirality of mononuclear nickel(II) complexes of (*R*,*R*)-**1** and (*S*,*S*)-**1** extends over the whole supramolecular structure. Although the chiral Schiff complexes are known to construct supramolecular helical structures,[3–7] to the best of our knowledge, the homochiral helix solely driven by the rare C–H···M interaction in neutral mononuclear metal complex has not yet been reported.

Results and Discussion

The optically pure ligands of (*R*,*R*)- and (*S*,*S*)-bis(pyrrol-2-ylmethyleneamino)cyclohexane were prepared by condensation of (*R*,*R*)-1,2-diaminocyclohexane mono-(+)-tartrate salt and (*S*,*S*)-1,2-diaminocyclohexane with 2-pyrrolealdehyde, respectively.[9] Under the base conditions, the two enantiomeric ligands were further reacted with $Ni^{II}(OAc)_2{\cdot}4H_2O$ at room temperature to afford neutral mononuclear complexes (*R*,*R*)-**1** and (*S*,*S*)-**1** with yields of 93 and 92%, respectively (Scheme 1). For comparison, racemic complex **1**[9b] was also synthesized.

Figure 1 shows the UV/Vis absorption and circular dichromism (CD) spectra of neutral complexes (*R*,*R*)-**1** and (*S*,*S*)-**1**. It was noted that the optically pure enantiomers of (*R*,*R*)-**1** $\{[\alpha]_D^{20} = -3832$ ($c = 0.0033$, CH_2Cl_2)$\}$ and (*S*,*S*)-**1** $\{[\alpha]_D^{20} = +3833$ ($c = 0.0032$, CH_2Cl_2)$\}$ show near mirror image behaviors in the circular dichroism (CD) spectra, while the absorption spectra are not distinguishable from each other. Correlated with the observed CD spectra, the absolute configuration of (*R*,*R*)-**1** and (*S*,*S*)-**1** can be subsequently assigned to Δ and Λ, respectively, in terms of the definition of IUPAC nomenclature[10a] and the reference method.[10b–10c]

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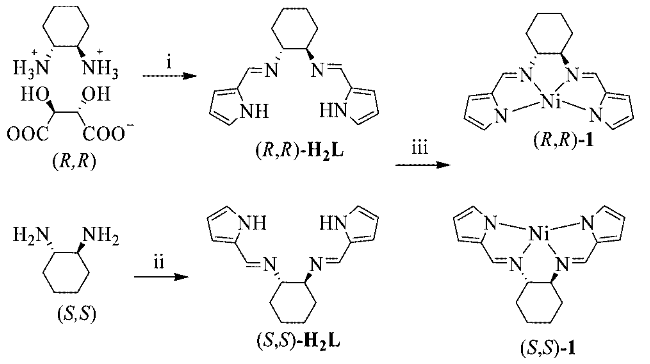


Scheme 1. Synthesis of (*R*,*R*)-**1** and (*S*,*S*)-**1** complexes. Reaction conditions: i) K_2CO_3, 2-pyrrolealdehyde, 80 °C, 4 h, water/ethanol (2:1); ii) 2-pyrrolealdehyde, reflux, 12 h, ethanol; iii) $Ni^{II}(OAc)_2\cdot 4H_2O$, KOH, r.t., 2 h, methanol.

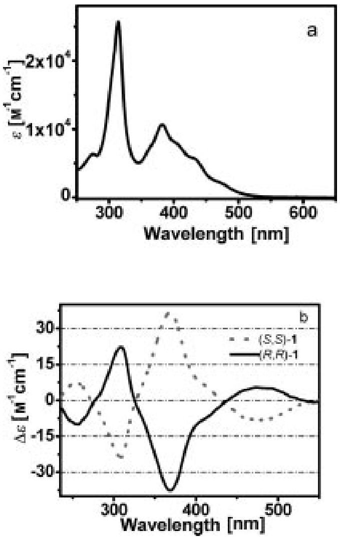
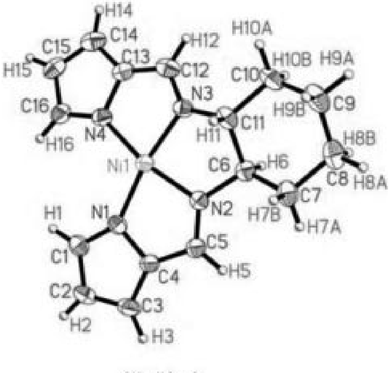
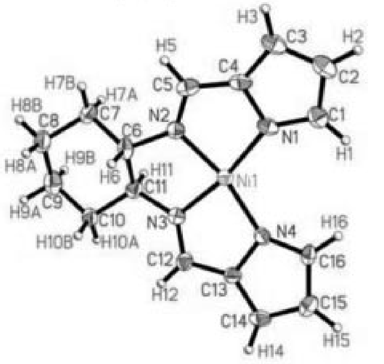


Figure 1. The absorption spectrum (a) and circular dichroism spectrum (b) of (*R*,*R*)-**1** (4.43×10^{-5} M) and (*S*,*S*)-**1** (3.68×10^{-5} M) in acetonitrile solution at room temperature.

Single crystals of (*R*,*R*)-**1**, (*S*,*S*)-**1**, and **1** were obtained by slow evaporation of a CH_2Cl_2/methanol solution. Red single crystals of these three complexes as needles were used for data collection with the use of a Bruker Smart 1000 X-ray diffractometer with Mo-K_α radiation. The crystals of (*R*,*R*)-**1** and (*S*,*S*)-**1** belong to the monoclinic crystal system and $P2_1$ space group, while **1** is the monoclinic crystal system and $P2_1/c$ space group. The crystallographic data for (*R*,*R*)-**1** and (*S*,*S*)-**1**, as well as **1** were listed in Table 2. Figure 2 shows the two neutral mononuclear (*R*,*R*)-**1** and (*S*,*S*)-**1** complexes. Each Ni^{II} center is four-coordinate to four N atoms from pyrrol-2-yl-cyclohexenediamine Schiff-base unit. The length of the Ni^{II}–N bond is in the range of 1.844–1.890 Å. The dative Ni^{II}–N(imine) bond lengths (1.844–1.867 Å) are comparable to those of other similar Ni^{II}–N bonds (1.843–1.895 Å) in the literature,[9b] but are shorter than those of the Ni^{II}–N(pyrrole) (1.877–1.890 Å). The conformation of *trans*-1,2-cyclohexyldiamine leads to a twisted conformation, where the cyclohexyl ring is in a stable chair conformation and the two pyrrol-2-yl units of same ligand adopt a *cis* conformation with dihedral angles of 18° (Ni1–N1–N2 and Ni1–N4–N3) in (*R*,*R*)-**1** and 18.3° (Ni1–N1–N2 and Ni1–N4–N3) in (*S*,*S*)-**1**, respectively. The dihedral angles in (*R*,*R*)-**1** and (*S*,*S*)-**1** implied that the Ni^{II} center has a small deviation from the square-planar coordination geometry. Evidently, the configuration of (*R*,*R*)-**1** and (*S*,*S*)-**1** can be definitely evaluated as Δ and Λ with respect to the C_2-axis, which is consistent with their assignments on the basis of CD spectra.



(*R*,*R*)-1



(*S*,*S*)-1

Figure 2. Crystal structures of (*R*,*R*)-**1** and (*S*,*S*)-**1** with atom numbering.

A noticeable feature of (*R*,*R*)-**1** and (*S*,*S*)-**1** lies in the weak intermolecular C–H···Ni^{II} interactions in the molecular packing (Figure 3). As in the case of (*R*,*R*)-**1**, each ligand uses its hydrogen atoms to bind the nickel(II) center of the others. Because the two pyrrol-2-yldiamine units of the same ligand adopt a *cis* conformation and the C–N-(imine) bonds in the rigid *trans*-1,2-cyclohexyl moiety are arranged reciprocally, the unit cell contains three different intermolecular C–H···Ni^{II} interactions in the crystal of (*R*,*R*)-**1**. As sketched in Figure 3, each molecule of (*R*,*R*)-**1** is stacking with two adjacent molecules via the intermolecular C–H···Ni^{II} interactions. Table 1gives the structural parameters related to the C–H···Ni^{II} interactions in (*R*,*R*)-**1** and (*S*,*S*)-**1**. The Ni^{II}···H distance is similar to that recently observed by Pal. et al., who demonstrated the presence of intramolecular apical C–H···Ni^{II} interactions in square-planar nickel(II) complexes with dianionic tridentate ligands and 2-phenylimidazole.[11] The intermolecular contacts of 3.002 Å at C43A–H43A···Ni1A, 3.025 Å at

C6A–H6A···Ni3A, and 3.127 Å at C7A–H7BA···Ni3B with the C–H···Ni$^{\mathrm{II}}$ angle of 141.1°, 166.9°, and 141.5°, respectively, lead to the formation of helical assemblies with different pitches in the helix. Two sets, four complex fragments form one helix with a screw-pitch of 17.242 Å. The intermolecular metal···metal contacts are found to be 5.989 Å (Ni3A–Ni1A) and 8.621 Å (Ni1A–Ni3B), respectively. Obviously, the turn required to generate a perfect periodic self-assembly of (*R*,*R*)-**1** in a helical fashion is induced by the chirality of the building block coupled with the weak intermolecular C–H···Ni$^{\mathrm{II}}$ interactions. An *M* handedness can be clearly assigned to complexes (*R*,*R*)-**1** when viewed along the *b* axis. At the molecular level, this local chirality translates throughout the crystal into the formation of only left-handed (*M*) helix at the supramolecular level. The path of the helix can be easily traced by following the C–H···Ni$^{\mathrm{II}}$ interactions counterclockwise around the screw axis of the helix. A similar self-assembly pattern exists in the crystal packing of (*S*,*S*)-**1**. The only difference is the opposite direction presented in which the intermolecular C–H···Ni$^{\mathrm{II}}$ interactions show a clockwise turn around the screw axis to give a right-handed (*P*) helix. A comparison of the two space-filling models evidences the near mirror image behavior of the (*R*,*R*)-**1** and (*S*,*S*)-**1** helices (Figure 3), indicating they are enantiomeric from a supramolecular point of view.

Table 1. Parameters for C–H···Ni$^{\mathrm{II}}$ intermolecular interactions in three Ni$^{\mathrm{II}}$ complexes.

Complex	C–H···Ni$^{\mathrm{II}}$	d[a] [Å]	d[b] [Å]	D[c] [Å]	θ[d] [°]
(*R*,*R*)-**1**	C43A–H43A···Ni1A	0.98	3.002	3.817	141.1
	C7A–H7BA···Ni3B	0.97	3.025	3.976	166.9
	C6A–H6A···Ni3A	0.98	3.127	3.942	141.5
(*S*,*S*)-**1**	C22B–H22B···Ni3B	1.00	3.140	3.952	139.3
	C23B–H23C···Ni3A	0.99	2.983	3.945	164.2
	C38A–H38A···Ni2A	1.00	2.978	3.792	139.2
1	C14D–H14D···Ni1I	0.95	3.154	3.954	156.4
	C11D–H11D···Ni1B	1.00	2.884	3.721	141.8
	C14I–H14I···Ni1E	0.95	3.154	3.954	156.4
	C11B–H11B···Ni1D	1.00	2.884	3.721	141.8

[a] For C–H distance. [b] For H···Ni$^{\mathrm{II}}$ distance. [c] For C–Ni$^{\mathrm{II}}$ distance. [d] C–H···Ni$^{\mathrm{II}}$ angle.

To provide more evidence for the unique intermolecular C–H···Ni$^{\mathrm{II}}$ interaction, the self-assembly manner presented in racemic complex **1** was also investigated. Apparently, the situation is quite different from that in (*R*,*R*)-**1** and (*S*,*S*)-**1**. Two molecules of (*R*,*R*)-**1** and (*S*,*S*)-**1** interact with each other in one unit cell via intermolecular C–H···Ni$^{\mathrm{II}}$ interactions (Figure 4). However, one H atom from the pyrrole

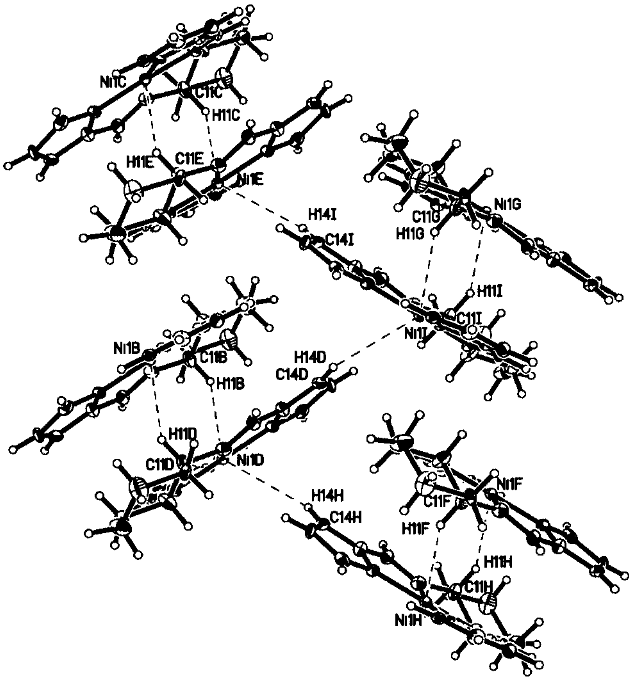


Figure 4. Crystal packing diagram of racemic **1** with atom numbering.

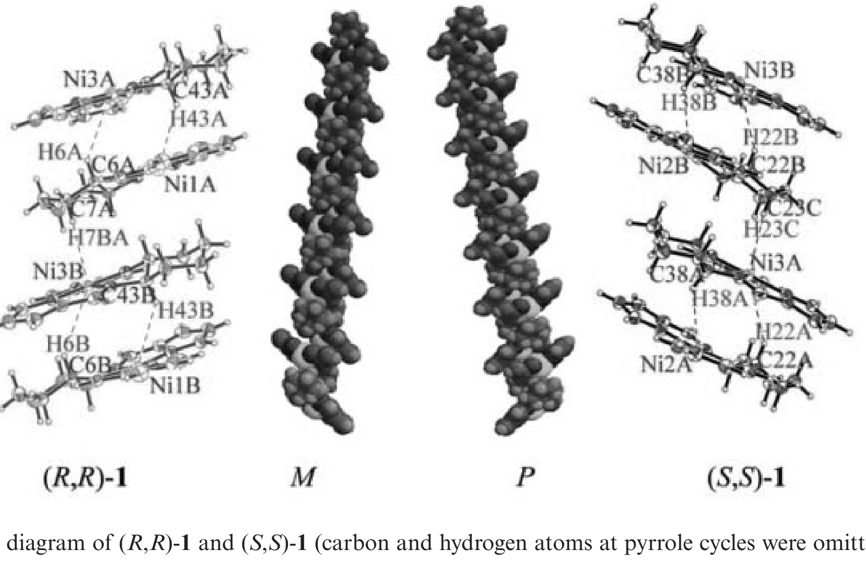


Figure 3. Crystal packing diagram of (*R*,*R*)-**1** and (*S*,*S*)-**1** (carbon and hydrogen atoms at pyrrole cycles were omitted for clarity in space-filling view).

ring rather than from the 1,2-cyclohexyl unit in one molecule is bound to the Ni center of the other. Since the intermolecular C–H···Ni^{II} distance of 2.884 Å at C11D–H11D···Ni1B and 2.884 Å at C11B–H11B···Ni1D in complex **1** are appreciably shorter than those of either (*R*,*R*)-**1** or (*S*,*S*)-**1**, homochiral *M* and *P* helices were not observed in the crystal packing of **1**. Alternatively, the racemic unit cell of complex **1** is assembled to display a picture that is far from that observed for the (*R*,*R*)-**1** and (*S*,*S*)-**1** helices.

Conclusions

We demonstrated that the rare C–H···Ni^{II} interaction is responsible for controlling self-assembly of neutral, chiral, mononuclear complexes of (*R*,*R*)-**1** and (*S*,*S*)-**1**, leading to the formation of *M* and *P* helices of (*R*,*R*)-**1** and (*S*,*S*)-**1** in crystal lattices. Extending the scope of the intriguing complexes and exploring their applications are ongoing in our laboratory.

Experimental Section

All synthetic regents were of analytical grade and used as received. The solvents used for spectroscopic measurements were purified according to the literature method.[12] Melting points were determined with a Yanaco MP-500 micro-melting point apparatus. NMR spectra were recorded with a Bruker Avance dpx 400 MHz instrument using TMS as an internal standard. Mass spectra were obtained with Bruker APEX II spectrometers. Elemental analyses were performed with a FLASH EA1112 elemental analyzer. The UV/Vis absorption spectra of these compounds were recorded using a Shimadzu 1601 spectrophotometer. The circular dichroism (CD) spectra were measured with a JASCO J-810 spectropolarimeter. The values of specific rotation were measured with a Perkin–Elmer 341LC polarimeter.

(*R*,*R*)-Bis(pyrrol-2-ylmethyleneamino)cyclohexane [(*R*,*R*)-H$_2$L]: A 100-mL two-necked flask equipped with a magnetic stirrer, a reflux condenser, and an addition funnel was charged with (*R*,*R*)-1,2-diaminocyclohexane mono-(+)-tartrate salt (2.64 g), K_2CO_3 (2.79 g) and distilled water/ethanol (2:1, 60 mL). The mixture was heated to 80°C, and then 2-formylpyrrole (1.9 g) in ethanol (10 mL) was added slowly over 20 min. The yellow solution was heated at reflux for 2 h before distilled water (20 mL) was added. The solution was placed in an ice bath for 4 h to afford a white solid, which was collected by vacuum filtration, washed with water, and dried under vacuum. The product was further recrystallized from ethanol to give optically pure (*R*,*R*)-**H$_2$L**. Yield: 2.2 g, 78%. M.p. 204 °C (dec.). $[\alpha]_D^{20}$ = –1041 (*c* = 0.0023, CH_3OH). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.36–1.79 (m, 8 H), 3.01–3.05 (m, 2 H), 6.17 (dd, *J* = 2.5, 2.7 Hz, 2 H), 6.36 (d, *J* = 2.5 Hz, 2 H); 6.81 (s, 2 H), 7.77 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.92, 34.34, 72.87, 109.69, 114.55, 122.01, 130.66, 152.32 ppm. MS (EI): *m*/*z* = 268. $C_{16}H_{20}N_4 \cdot H_2O$ (286.4): calcd. C 67.11, H 7.74, N 19.56; found C 66.96, H 7.75, N 19.40.

(*S*,*S*)-Bis(pyrrol-2-ylmethyleneamino)cyclohexane [(*S*,*S*)-H$_2$L]: 2-Formylpyrrole (6 mmol) and (*S*,*S*)-1,2-diaminocyclohexane (3 mmol) were dissolved in ethanol (35 mL). The yellow solution was heated at reflux for 12 h under an atmosphere of argon. The solvent was removed by evaporation. The residue was further recrystallized from 95% ethanol to give optically pure (*S*,*S*)-**H$_2$L**. Yield: 0.58 g, 68%. M.p. 206 °C (dec.). $[\alpha]_D^{20}$ = +1040 (*c* = 0.0021, CH_3OH). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.36–1.79 (m, 8 H), 3.01–3.05 (m, 2 H), 6.17 (dd, *J* = 2.5, 2.7 Hz, 2 H), 6.36 (d, *J* = 2.5 Hz, 2 H); 6.81 (s, 2 H), 7.77 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.93, 34.33, 72.88, 109.68, 114.57, 122.02, 130.66, 152.30 ppm. MS (EI): *m*/*z* = 268. $C_{16}H_{20}N_4 \cdot H_2O$ (286.4): calcd. C 67.11, H 7.74, N 19.56; found C 66.98, H 7.73, N 19.42.

(*R*,*R*)-Bis(pyrrol-2-ylmethyleneamino)cyclohexane Nickel(II) Complex [(*R*,*R*)-1]: A mixture of optically pure (*R*,*R*)-**H$_2$L** (1 mmol) and $Ni^{II}(OAc)_2 \cdot 4H_2O$ (1.1 mmol) in methanol (30 mL) was stirred for 10 min at r.t. With the addition of KOH (2 mmol) in methanol (10 mL), the mixture was stirred for another 2 h accompanying the formation of a precipitate, which was collected by suction filtration followed by washing with distilled water and methanol. Recrystallization from dichloromethane/methanol produced the expected red crystals. Yield: 301 mg, 93%. M.p. 272 °C (dec.). $[\alpha]_D^{20}$ = –3832 (*c* = 0.0033, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.27–1.29 (m, 4 H, CH_2), 1.80–1.81 (br. s, 2 H, CH_2), 2.19–2.20 (br. s, 2 H, CH_2), 3.41–3.42 (br. s, 2 H, CH), 6.12 (dd, *J* = 3.6, 3.4 Hz, 2 H, pyrrole-βH), 6.58 (d, *J* = 3.6 Hz, 2 H, pyrrole-γH), 6.80 (s, 2 H, pyrrole-αH), 7.17 (s, 2 H, imine-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.1, 28.0, 70.4, 111.3, 116.3, 136.0, 142.9, 154.0 ppm. HRMS (FAB): calcd. for $C_{16}H_{18}N_4Ni$ $[M + H]^+$ 324.0878; found 324.0877. $C_{16}H_{18}N_4Ni$ (324.1): calcd. C 59.12, H 5.58, N 17.24; found C 58.94, H 5.58, N 17.28.

(*S*,*S*)-Bis(pyrrol-2-ylmethyleneamino)cyclohexane Nickel(II) Complex [(*S*,*S*)-1]: The synthetic procedure was similar to that of (*R*,*R*)-**1** except for optically pure (*S*,*S*)-**H$_2$L** was used. Yield: 298 mg, 92%. M.p. 268 °C (dec.). $[\alpha]_D^{20}$ = +3833 (*c* = 0.0032, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.27–1.29 (m, 4 H, CH_2); 1.80–1.81 (br. s, 2 H, CH_2), 2.19–2.20 (br. s, 2 H, CH_2), 3.41–3.42 (br. s, 2 H, CH), 6.12 (dd, *J* = 3.6, 3.5 Hz, 2 H, pyrrole-βH), 6.57 (d, *J* = 3.6 Hz, 2 H, pyrrole-γH), 6.80 (s, 2 H, pyrrole-αH), 7.17 (s, 2 H, imine-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.1, 27.9, 70.5, 111.3, 116.2, 135.6, 143.0, 154.2 ppm. HRMS (FAB): calcd. for $C_{16}H_{18}N_4Ni$ $[M + H]^+$ 324.0878; found 324.0870. $C_{16}H_{18}N_4Ni$ (324.1): calcd. C 59.12, H 5.58, N 17.24; found C 58.94, H 5.48, N 17.30.

X-ray Crystallographic Studies: Crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated solution of dichloromethane/methanol. Accurate unit cell parameters were determined by least-squares fit of 2θ values, measured for 200 strong reflections, and intensity data sets were measured with a Bruker Smart 1000 CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) at 294 K. The intensities were corrected for Lorentz and polarization effects. All structures were analyzed by direct methods. The non-hydrogen atoms were located in successive difference Fourier synthesis. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 (SHELXL-97).[13] The hydrogen atoms were added theoretically and treated as riding on the concerted atoms. Crystallographic data and experimental details for structure analyses are summarized in Table 2. CCDC-638806, -638807, and -638808 [for (*R*,*R*)-**1**, (*S*,*S*)-**1**, and **1**, respectively] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystallographic data and structure refinement summary for (*R*,*R*)-**1**, (*S*,*S*)-**1**, and **1**.

Compound	(*R*,*R*)-**1**	(*S*,*S*)-**1**	**1**
Empirical formula	$C_{16}H_{18}N_4Ni$	$C_{16}H_{18}N_4Ni$	$C_{16}H_{18}N_4Ni$
Formula weight	325.05	325.05	325.05
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1/c$
a [Å]	17.458(2)	17.2362(17)	21.3123(18)
b [Å]	8.6212(10)	8.5702(8)	8.7642(8)
c [Å]	21.366(3)	21.305(3)	16.9496(12)
α [°]	90	90	90
β [°]	111.681(2)	111.733(6)	111.633(7)
γ [°]	90	90	90
Volume [$Å^3$]	2988.2(6)	2923.5(5)	2942.9(4)
Z, Calculated density [$g\,cm^{-3}$]	8, 1.445	8, 1.477	8, 1.467
Absorption coefficient [mm^{-1}]	1.297	1.325	1.317
F (000)	1360	1360	1360
Crystal size [mm]	0.22 × 0.18 × 0.10	0.18 × 0.14 × 0.10	0.20 × 0.14 × 0.12
θ Range for data collection [°]	1.03 to 26.47	1.03 to 27.79	2.40 to 25.00
Limiting indices	$-19 \le h \le 21$ $-8 \le k \le 10$ $-26 \le l \le 24$	$-22 \le h \le 21$ $-11 \le k \le 11$ $-27 \le l \le 27$	$-25 \le h \le 25$ $-10 \le k \le 10$ $-20 \le l \le 20$
Reflections collected/unique	17099/10244 [*R*(int) = 0.0323]	27420/13723 [*R*(int) = 0.0425]	21327/5170 [*R*(int) = 0.1324]
Completeness to θ	99.9%	99.6%	99.7%
Data/restraints/parameters	10244/1/758	13723/1/759	5170/0/380
Goodness-of-fit on F^2	1.016	0.990	0.912
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0379$, $wR2 = 0.0833$	$R1 = 0.0404$, $wR2 = 0.0810$	$R1 = 0.0807$, $wR2 = 0.1200$
Absolute structure parameter	–0.050(17)	0.024(12)	–
Extinction coefficient	0.0044(2)	0.00194(17)	0.033(2)
Largest diff. peak/hole [$e\,Å^{-3}$]	0.286/–0.424	0.567/–0.400	1.149/–1.361

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