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PAPER

Chirality at metal and helical ligand folding in optical isomers of chiral *bis*(napthaldiminato)nickel(II) complexes†

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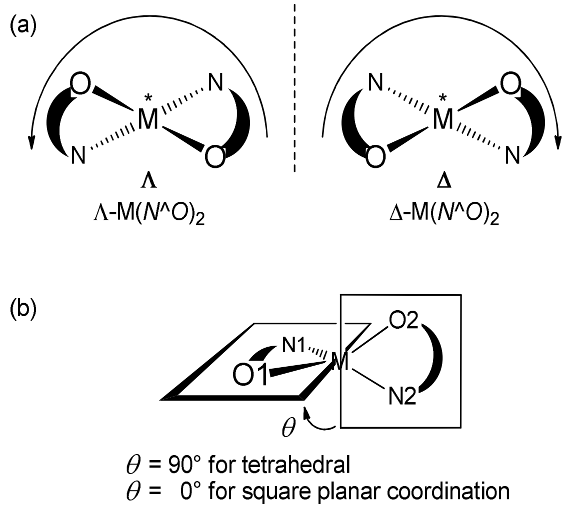
Enantiopure *bis*[{(*R* or *S*)-N-1-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}]nickel(II) complexes {Ar = C_6H_5 (**1*R*** or **1*S***), *p*-OMeC_6H_4 (**2*R*** or **2*S***), and *p*-BrC_6H_4 (**3*R*** or **3*S***)} are synthesized from the reactions between (*R* or *S*)-N-1-(Ar)ethyl-2-oxo-1-naphthaldimine and nickel(II) acetate. Circular-dichroism spectra and their density-fuctional theoretical simulation reveal the expected mirror image relationship for the enantiomeric pairs **1*R***/**1*S*** and **3*R***/**3*S*** in solution. CD spectra are dominated by the metal-centered Λ- and Δ-chirality of non-planar four-coordinated nickel, this latter being in turn dictated by the ligand chirality. Single crystal structure determinations for **1*R*** and **1*S*** show that there are two symmetry-independent molecules (**A** and **B**) in each asymmetric unit to give a Z' = 2 structure. Two asymmetric and chiral bidentate *N^O*-chelate Schiff base ligands coordinate to the nickel atom in a distorted square planar N_2O_2-coordination sphere. The conformational difference between the symmetry-independent molecules arises from "up-or-down" folding of the naphthaldiminato ligand with respect to the coordination plane, which creates right- (*P*) or left-handed (*M*) helical conformations. Overall, the combination of ligand chirality, chirality at metal and ligand folding gives rise to discrete metal helicates of preferred helicity in a selective way. Cyclic voltammograms (CV) show an oxidation wave at *ca.* 1.30 V for $[Ni(L)_2]/[Ni(L)_2]^+$ couple, while a reduction wave at *ca.* −0.35 V for $[Ni(L)_2]/[Ni(L)_2]^-$ couple in acetonitrile.

Introduction

Chiral metal coordination complexes are the subject of continuous study due to their fascinating structures, and enormous potential applications such as molecular recognition, non-linear optical materials, asymmetric catalysis and enantiomeric separation, and so on.[1,2] One of the possible ways of generating enantiopure chiral-at-metal complexes is the employment of chiral chelating ligands, which may then transfer their chirality to the metal centre(s) generating right- (Δ) or left-handed (Λ) helical structures in a stereocontrolled way.[3] Use of achiral chelating ligands usually results in a racemic mixture of left- and right-handed Δ/Λ-optical isomers.[4] Of special interests in the context of supramolecular chemistry are metal helicates, that is, metal complexes where one or more ligand "strands" wrap around one or more metal centre in a helical fashion.[5] In tetrahedral or distorted square-planar complexes the metal-centered chirality (Λ vs. Δ) can be induced with a C_2-symmetric structure by the use of an asymmetric ligand A^B to give $M(A^B)_2$ complexes (cf. Scheme 1).[6,7] An enantiomerically pure chelate ligand (*R* or *S*-A^B) often leads to the preferential formation of one diastereomer with absolute configurations of Λ(*R*,*R*) or Δ(*S*,*S*), while racemic ligand gives both diastereomers {e.g. Λ(*R*,*R*) and Δ(*S*,*S*)}.[6,7,8,9]



Scheme 1. Definition of (a) Λ/Δ chirality at the metal centre and (b) dihedral angle *θ* quantifying the deviation from tetrahedral or square planar geometry.

We have recently given attention to the phenomenon of helicity (*P* vs. *M*) and induced metal-centered chirality (Λ vs. Δ) in the complexes formed by the enantiopure amino acids and Schiff base ligands with Rh(I),[10,11] and Cu/Ni/Zn(II), respectively.[12,13,14,15] The most noteworthy finding in our studies is that the achiral *N*-phenylglycinate ligand coordinates to the $[Rh(\eta^4\text{-cod})(acetate)]_2$ and gives a racemic chiral $[Rh(\eta^4\text{-cod})(N\text{-phenylglycinate})]$ complex with the nitrogen atom becoming the stereogenic center upon metal coordination.[10,11] The crystal structures reveal a case of two-fold spontaneous resolution of a racemic mixture into two homochiral helical enantiomers (helicates), namely the right-(*P*)and left-handed (*M*)helical chain structure with the *S*- and *R*-*N*-phenylglycinate, respectively. Later, we have reported some examples of induced chirality at-metal-center with preferential formation of Λ or Δ-M configuration in distorted square planar $M(N,O\text{-chelate})_2$ (*N*,*O*-chelate = enantiopure Schiff base ligands; M = Cu, Ni, and Zn), which can be efficiently controlled by *R*- or *S*-chirality of the ligand.[12-14] Similarly, induced chirality at-metal-center in distorted square planar Cu/Zn(II) complexes with enantiopure or racemic amino alcohol based Schiff base ligands were reported.[15] In particular, we have reported for the first time an example of induced chirality at-nickel-centre (Δ vs. Λ) in distorted octahedral, dinuclear μ-aqua-*tetrakis*{(*R* or *S*)-N-1-

(Ar)ethyl-salicylaldiminato}-di-Λ- or Δ-nickel(II).[13]

The present paper reports the results of syntheses, spectroscopy, excited-state calculations and structural analyses of Z' = 2 helical structures of *bis*{(*R* or *S*)-N-1-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}nickel(II) {Ar = C_6H_5, *p*-OMeC_6H_4, and *p*-BrC_6H_4}. The present complexes are structurally simpler than the related octahedral dinuclear analogs[13], however, the specific folding of naphthaldiminato ligands around the metal centre gives rise to structurally intriguing discrete metal helicates.

Results and discussion

The enantiopure Schiff base ligands, (*R* or *S*)-N-1-(Ar)ethyl-2-oxo-1-naphthaldimine (*R* or *S*-HL), react with nickel(II)acetate to provide the *bis*[{(*R* or *S*)-N-1-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}]nickel(II) complexes {Ar = C_6H_5 (Ni-*R*-L1; **1*R*** or Ni-*S*-L1; **1*S***), *p*-OMeC_6H_4 (Ni-*R*-L2; **2*R*** or Ni-*S*-L2; **2*S***), and *p*-BrC_6H_4 (Ni-*R*-L3; **3*R*** or Ni-*S*-L3; **3*S***)} (Scheme 2). Vibrational spectra show the main characteristic band at 1617-1604 cm^{-1} for the νC=N stretching.[12-16,17] ESI-MS show the parent ion peak at *m*/*z* 607 (**1*R*** or **1*S***) and 667 (**2*R*** or **2*S***) for $[M+H]^+$ species, while EI-MS show this peak at *m*/*z* 764 (**3*R*** or **3*S***) for $[M]^+$. The spectra further show several ions peaks for the $[M\text{-HL}]^+$, $[\text{HL or HL+H}]^+$ and different fragmented ligand species (Table S1). ^{1}H NMR spectra (Figure S1) in $CDCl_3$ show a series of peaks expected for the C_2-symmetric diamagnetic four coordinated Ni(II)-complexes with square planar geometry (Experimental Section and Supporting Information).[11,13,18,19,20] Notably, the imine (C*H*N) protons display large coordination shifts and appear as broad resonances above 11 ppm. The signal broadening, also seen at a smaller extent for other resonances, is probably due to solution paramagnetism. This is a well-known phenomenon for Ni(II) salicylideneaminato-complexes with bulky *N*-substituents and has been explained with a fast equilibrium between a dominant singlet species and a minor triplet species triggered by geometrical distortion (toward a tetrahedral geometry) and/or molecular association.[21]

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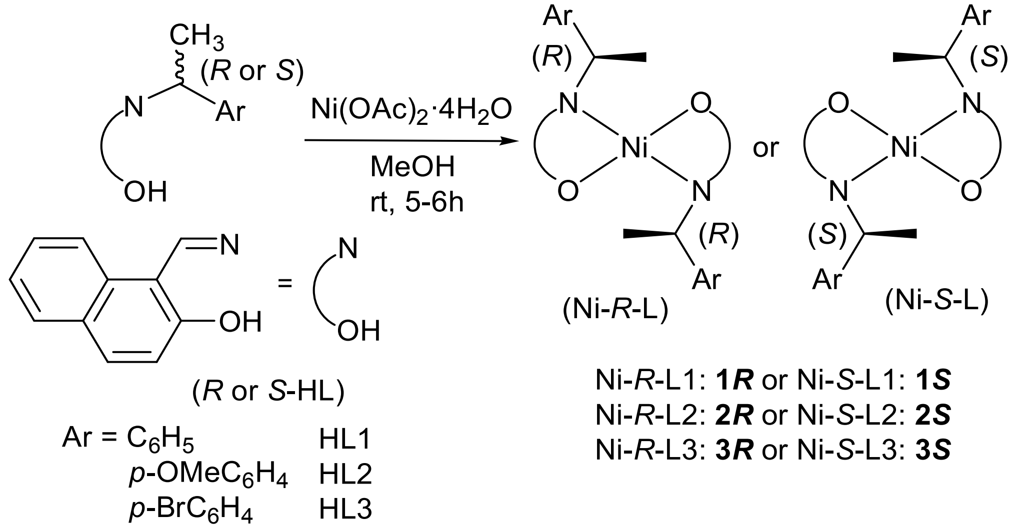


Scheme 2. Syntheses of the *bis*[{(*R* or *S*)-N-1-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}]nickel(II).

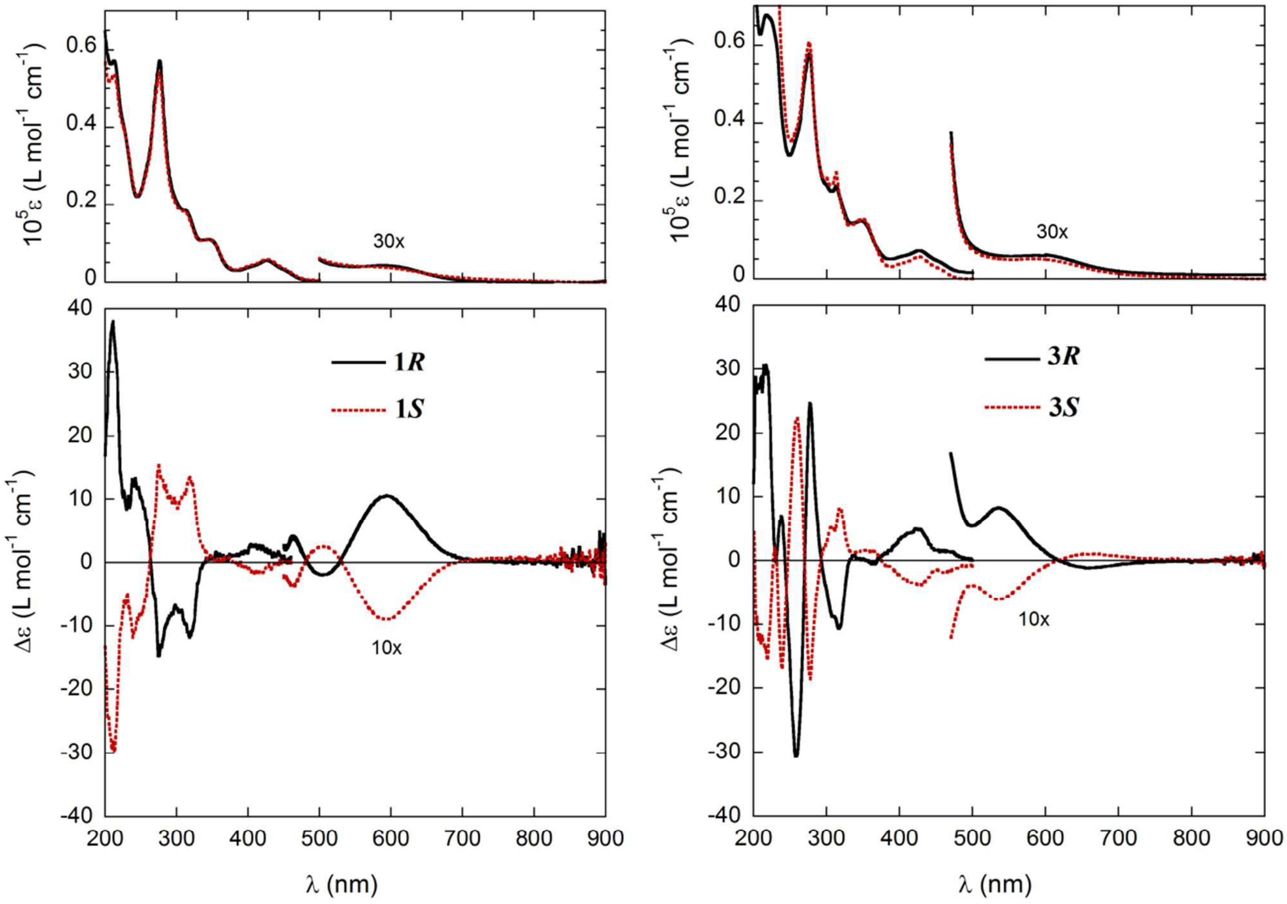


Figure 1. UV-vis. and CD spectra of **1*R*** (0.76 mM), **1*S*** (0.79 mM) (left), and **3*R*** (1.95 mM), **3*S*** (1.96 mM) (right) in cyclohexane; cell path-length: 0.1 mm, 200–500 nm; 5 mm, 425–600 nm; 10 mm, 400–900 nm.

Electronic Spectra

UV-vis absorption and CD spectra of the complexes **1** and **3** measured in cyclohexane are shown in Figure 1 and summarized in Table 1. All absorption spectra show consistent similarities over the whole measured range of 200-900 nm. In the visible region, there is a weak broad band around 600 nm followed by three bands of increasing intensity between 380-480, 330-380 and around 310 nm, respectively. They are followed by two more intense bands at 250-300 and below 250 nm. The band around 600 nm is due to the superposition of several metal-centred transitions typical of the Ni^{2+} core. The next bands in the UV region (<480 nm) involve a complex combination of several transitions, centred on both the metal and the ligands, as will be discussed below.

Electronic CD spectra of the enantiomeric couples **1*R*/1*S*** and **3*R*/3*S*** show the expected mirror-image relationship (Figure 1 and Table 1) in cyclohexane. CD spectra display a larger variation between the two compounds than the absorption spectra and also in comparison with the analogue Cu(II)-complexes.[12] In particular, in the visible range there is no distinctive feature immediately related to the ligand configuration for both **1** and **3**. The only consistent signals are in the UV region, and they are (for *R* configuration, Figure 1 and Table 1) the weak positive band between 400-450 nm, the stronger negative band at 300-330 nm, and the strong positive band below 220 nm.

We also measured solid-state CD spectra on crystalline samples of compound **1**, but found them not fully reproducible. Moreover, in the case of the analogous Cu complexes,[12] we demonstrated that solid-state CD spectra are dominated by inter-crystalline couplings and do not reflect in a simple way the molecular conformation.

Simulating the solution CD spectra of Ni complexes **1-3** by means of CD calculations is a laborious task because of the inherent complexity of the system[22] and the uncertainty of the solution structures. Therefore, the work described in the following aimed mainly at establishing the relationship between the observed CD spectra and the chirality at both carbon centres and metal ion (if any), in analogy with our previous work on Cu analogues.[12] Although the solid-state structures of **1*R*** and **1*S*** show only a faint chirality at the Ni atoms (see below), the situation in solution may in principle be different. The chirality at the metal centre is defined as shown in Scheme 1a, and the distortion from an ideal tetrahedral or square-planar geometry can be quantified by the dihedral angle θ between the two planes formed by the donor atoms with the metal atom, that is, N1–M–O1 and N2–M–O2 (Scheme 1b). Starting from the X-ray structure of **1*R***, we investigated the solution conformation of this complex by means of a conformational search with molecular mechanics and DFT geometry optimizations at B3LYP/6-31G(d) level (see Computational Section). The resulting most stable structure showed a small but detectable angle $\theta = -10.8°$ corresponding to **Λ-Ni-1*R*** chirality, and resembled strongly molecule **A** found in the X-ray (inset in Figure 2A); other conformations had much higher energies and were neglected. Starting from the same complex, the chirality at the metal centre was inverted and the same conformational search/geometry optimization procedure was applied. The set of structures with **Δ-Ni-1*R*** chirality thus obtained showed two low-energy conformations, one (more stable) with $\theta = 15.0°$ and the second (less stable by 0.16 kcal/mol) with $\theta = 9.0°$ (see Supporting Information). Interestingly, the lowest-energy **Λ-Ni-1*R*** structure was more stable by about 1.7 kcal/mol than the **Δ-Ni-1*R*** one. Thus, a small but non-negligible diastereomeric preference in favour of the **Λ-Ni-1*R*** isomer is predicted, similarly to what observed for the Cu analogues.[12] To confirm such finding, CD calculations were run with the TDDFT method[23] at B3LYP/TZVP level on the above described structures (Figure 2). The most striking observation from Figure 2 is that the CD spectra calculated for **Λ-Ni-1*R*** and **Δ-Ni-1*R*** are almost the mirror image of each other on a wide wavelength range. This demonstrates that the CD spectrum in solution is dominated by the metal chirality, this latter being in turn dictated by the ligand chirality. Second, the CD spectrum calculated for **Λ-Ni-1*R*** is in reasonable agreement with the experimental one for compound **1*R***. As said above, a perfect agreement cannot be expected because of the system complexity and the very large number of transitions concurring to the spectrum (80 excited states were included in the TDDFT calculations, which are intrinsically poorly accurate for high-lying transitions).[24] The comparison between experimental and calculated CD spectra allows us to confirm that the complex obtained from ligand ***R*-L1** assumes a predominant **Λ-Ni-1*R*** configuration in solution, and the same is inferred for the remaining ligands.

We have already stressed[12,13] that for d-metal complexes containing chromophoric ligands rich of transitions, such as compounds **1-3**, a straight forward assignment of electronic spectra in terms of purely metal- or ligand-centred transitions is not possible. On the basis of orbital and population analysis on compound **1*R*** at B3LYP/TZVP level, the simplified assignment shown in Table 2 was reached, concerning only the transitions most contributing to the CD spectrum above 300 nm. It is important to notice, however, that every transition derives from many single excitations, and there is no clear separation between metal-centred and ligand-centred transitions, because several metal-centred transitions occur deeply in the UV region of the spectrum.

Table 1. UV-vis. and CD spectral data of **1*R*/1*S*** and **3*R*/3*S*** in cyclohexane; cell path-length: 0.1 mm (200-500 nm); 5-10 mm (400-900 nm) at 20 ^{o}C.

Compounds	Spectra	Bands[a]
1*R*/1*S*	UV-vis.	588 (vw), 427 (m), 345 (s), 312 (s), 276 (vs), and 212 (vs) nm
3*R*/3*S*	UV-vis.	595 (vw), 425 (m), 348 (s), 312 (s), 277 (vs), and 220 (vs) nm
1*R*/1*S*	CD	590 (+/–, w), 505 (–/+, vw), 460 (+/–, vw), 410 (+/–, w), 317 (–/+, s), 276 (–/+, s), 240 (+/–, s), and 210 (+/–, vs) nm
3*R*/3*S*	CD	660 (–/+, vw), 534 (+/–, w), 425 (+/–, s), 313 (–/+, s), 278 (+/–, vs), 256 (–/+, vs), 237 (+/–, m), and 213 (+/–, vs) nm

[a] vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

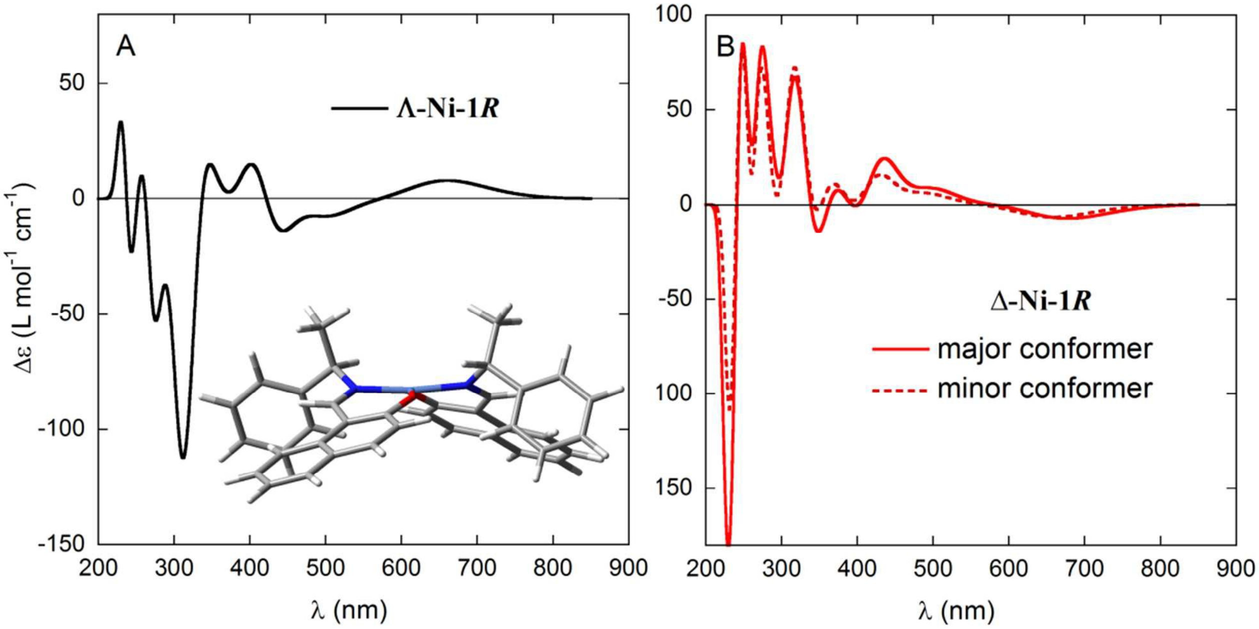


Figure 2. CD spectra calculated at the B3LYP/TZVP//B3LYP/6-31G(d) level for the two diastereomers **Λ-Ni-1*R*** (left, conformation shown in the inset) and **Δ-Ni-1*R*** (right, two conformations shown in Figure S3). Gaussian band shape with exponential bandwidth σ = 0.2 eV.

Table 2. Main transitions calculated for the **Λ-Ni-1*R*** complex with B3LYP/TZVP//B3LYP/6-31G(d), contribution to the first observed CD bands, and simplified assignment.

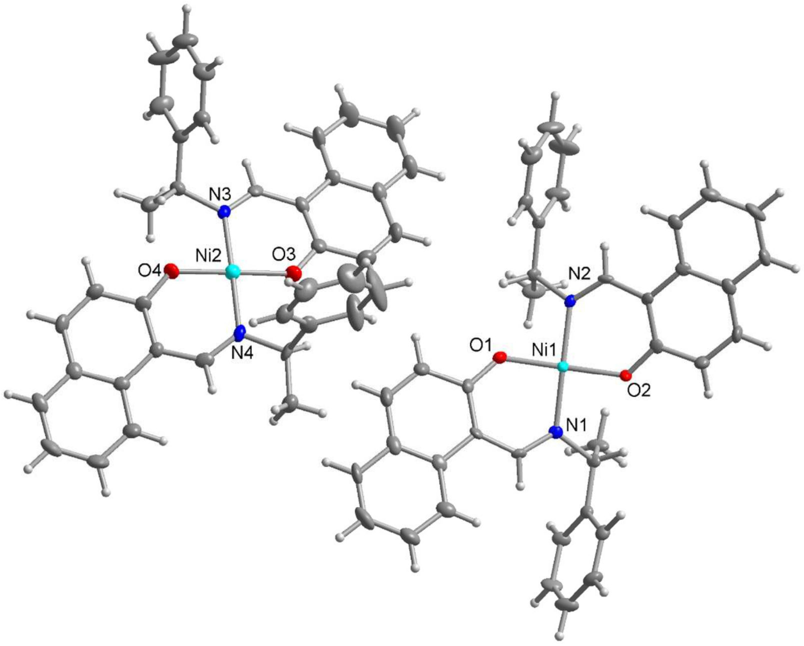
Exc. state	Calculated transition wavelength (nm)	Observed CD band (maximum wavelength, nm, and sign)	Assignment [(a)]
1	660	590 (+)	M-M
3	514	505 (–)	M-M, L-M, CT
4	498		CT, M-M
5	428		M-M
6	414	460 (+)	M-M
7+8	359	410 (+)	M-M
9	344		M-M, L-M
10	336		M-M, L-M
13	322	317 (–)	M-M
15	309		M-L

[(a)] Legend: M-M, metal d-d; L-M, ligand-to-metal; M-L, metal-to-ligand; CT, charge transfer; in order of importance.

Solid state structural studies

Single crystal X-ray structure determinations for Ni-*R*-L1 (**1*R***) and Ni-*S*-L1 (**1*S***) show that there are two symmetry-independent molecules in each asymmetric unit, that is, molecule **A** with Ni1 and molecule **B** with Ni2 centre in each unit. In each structure, two bidentate *N^O*-chelate Schiff base ligands coordinate to the nickel atom with a square planar N_2O_2-coordination sphere around the metal atom (Figure 3). The two nitrogen atoms (and subsequently the two oxygen atoms) are *trans* positioned. The Ni–O/N bond lengths and O–Ni–N bond angles are listed in Table 3 and are as expected from analogous Ni(II)-Schiff base complexes.[8,13] Despite the presence of aromatic rings in the complexes **Ni-*R*-L1** (**1*R***) and **Ni-*S*-L1** (**1*S***), there are no detectable π-π interactions[25] but intermolecular C-H···π contacts[26] are evident in the packings; a detailed analysis is reported in the Supporting Information.

Two symmetry-independent Ni-Schiff base molecules or, more correctly, two identical chemical formula units were found here in the structural asymmetric unit[27] to give a Z' = 2 structure. The definition of Z' is that it refers to the number of formula units in the unit cell (here 4) divided by the number of independent general positions (here 2).[28] Different reasons can lead to such Z' > 1 structures[29] : a structure stuck en-route to a more stable form,[28] that is, a crystal "on the way",[27,30,31,32] or strong and special supramolecular (e.g. hydrogen bonding) interactions between the two (or more) symmetry-independent units.[33, 34,35,36,37,38] A high Z' is also obtained when the molecule has different equi-energetic conformations, with these conformations co-existing in the crystal.[39,40] The chance for $Z' > 1$ is higher in non-centrosymmetric space groups with (enantiopure) chiral molecules which have difficulties to pack efficiently in the absence of centrosymmetry.[41]



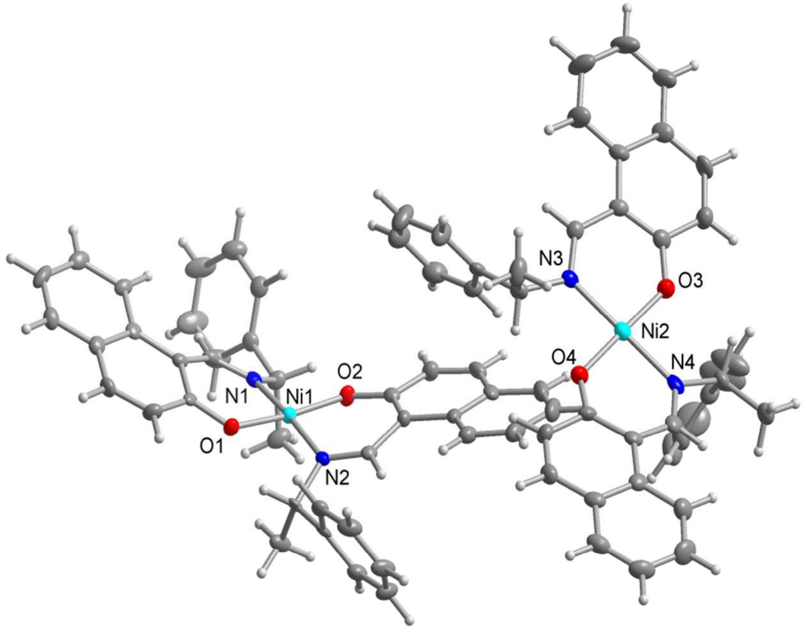
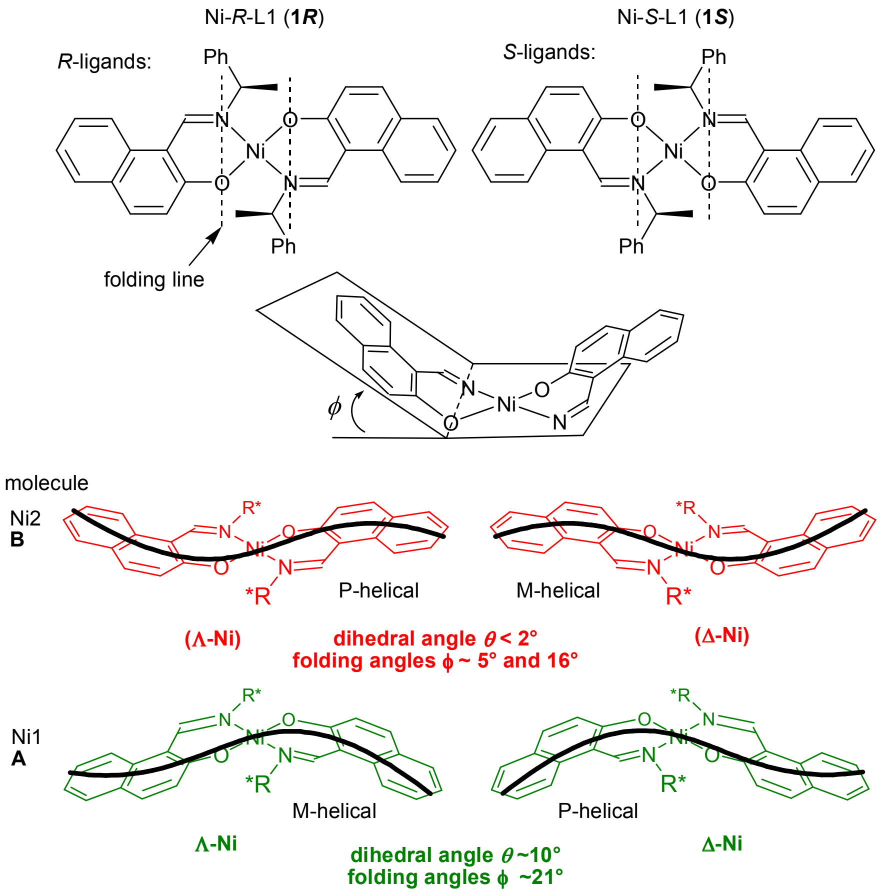


Figure 3. Structures of the two symmetry-independent molecules of the enantiomeric couple Ni-*R*-L1 (**1*R***) (above) and Ni-*S*-L1 (**1*S***) (below). Thermal ellipsoids are at the 70% level. See Table 3 for bond lengths and angles.

Table 3. Selected bond lengths (Å) and angles (°) in the compounds.[a]

Ni-*R*-L1 **(1*R*)**				Ni-*S*-L1 **(1*S*)**			
1*R* (A)				**1*S* (A)**			
Ni(1)-O(1)	1.848(2)	O(1)-Ni(1)-O(2)	172.73(10)	Ni(1)-O(1)	1.840(3)	O(1)-Ni(1)-O(2)	172.94(8)
Ni(1)-O(2)	1.850(2)	O(1)-Ni(1)-N(1)	92.16(11)	Ni(1)-O(2)	1.835(2)	O(1)-Ni(1)-N(1)	91.94(10)
Ni(1)-N(1)	1.908(3)	O(2)-Ni(1)-N(1)	88.35(11)	Ni(1)-N(1)	1.909(3)	O(2)-Ni(1)-N(1)	88.44(10)
Ni(1)-N(2)	1.914(3)	O(1)-Ni(1)-N(2)	88.39(11)	Ni(1)-N(2)	1.901(3)	O(1)-Ni(1)-N(2)	88.43(10)
		O(2)-Ni(1)-N(2)	92.01(11)			O(2)-Ni(1)-N(2)	92.08(10)
		N(1)-Ni(1)-N(2)	172.85(11)			N(1)-Ni(1)-N(2)	172.72(12)
1*R* (B)				**1*S* (B)**			
Ni(2)-O(3)	1.818(2)	O(3)-Ni(2)-O(4)	179.39(12)	Ni(2)-O(3)	1.817(3)	O(3)-Ni(2)-O(4)	179.33(10)
Ni(2)-O(4)	1.828(2)	O(3)-Ni(2)-N(3)	92.08(11)	Ni(2)-O(4)	1.823(3)	O(3)-Ni(2)-N(3)	92.01(10)
Ni(2)-N(3)	1.946(3)	O(4)-Ni(2)-N(3)	88.52(11)	Ni(2)-N(3)	1.935(3)	O(4)-Ni(2)-N(3)	88.6(1)
Ni(2)-N(4)	1.963(3)	O(3)-Ni(2)-N(4)	88.74(11)	Ni(2)-N(4)	1.953(3)	O(3)-Ni(2)-N(4)	88.8(1)
		O(4)-Ni(2)-N(4)	90.66(11)			O(4)-Ni(2)-N(4)	90.6(1)
		N(3)-Ni(2)-N(4)	178.02(12)			N(3)-Ni(2)-N(4)	178.11(11)

[a] **A** and **B** refer to the two symmetry independent molecules in each of the structure.



Scheme 3. Schematic illustration of the non-planar, skewed *bis*(naphthaldiminato) N_2O_2 ligand arrangement around the nearly square-planar coordinated Ni atom in **1*R*** (left) and **1*S*** (right) and definition of the folding angle ϕ. The thick black line depicts the *P*- or *M*-helical arrangement from the envelope conformation in the $NiNOC_3$ chelate ring together with the curvature in the naphthaldiminato ligand. The round brackets indicated a faint chirality at Ni.

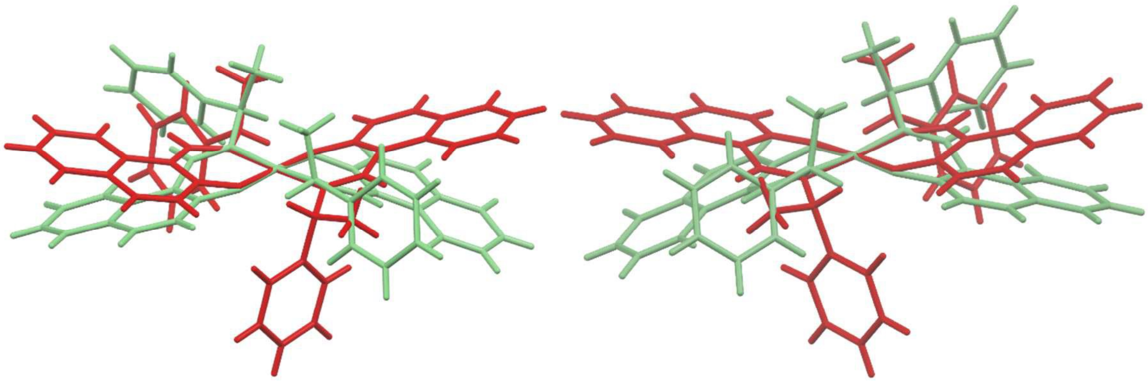


Figure 4. Overlay of the two symmetry independent molecules in Ni-*R*-L1 (**1*R***) (left) and Ni-*S*-L1 (**1*S***) (right). The Ni1 molecule **A** is shown in green, the Ni2 molecule **B** in red. The five atoms NiN_2O_2 were pairwise specified to orient the overlay which was managed with the "Structure overlay" option in Mercury 3.5.1 (copyright CCDC 2001-2014, http://www.ccdc.cam.ac.uk/mercury/).

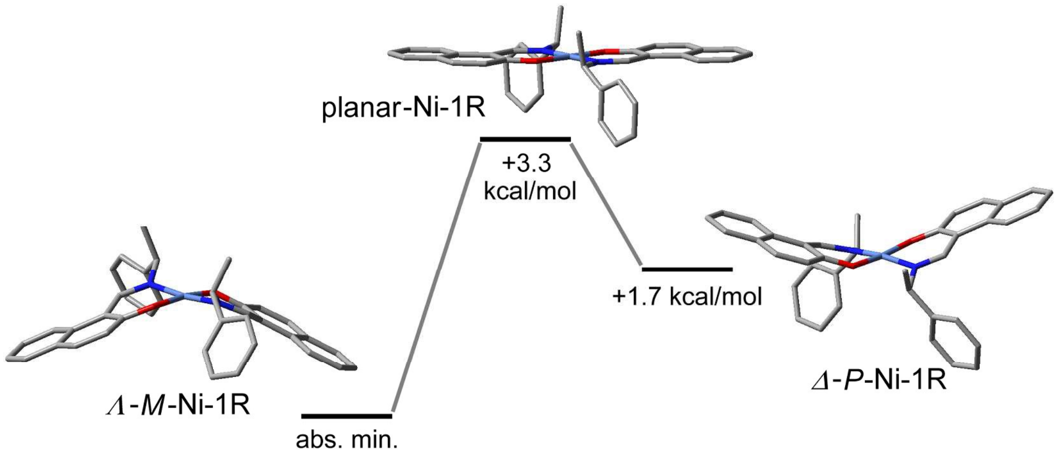


Figure 5. Sketch of the interconversion process between **Λ-Ni-1*R*** (*M*-helical) and **Δ-Ni-1*R*** (*P*-helical) structures in solution, passing through a planar intermediate (devoid of metal chirality and helicity). Geometry optimizations and energies calculated at B3LYP/ 6-31G(d) level; the middle structure was optimized by constraining the Ni(bis-naphthaldiminato) moiety into a planar conformation. Hydrogen atoms are omitted for clarity.

Table 4. Dihedral [a] and folding angles [c] for the two symmetry independent molecules (**A**, **B**) in Ni-*R*-L1 (**1*R***) and Ni-*S*-L1 (**1*S***), respectively.

Complexes (molecule)	chirality at Ni [a]	θ (°) [b] exp.	θ (°) [b] calc. [c]	ϕ (°) [d] exp.		ϕ (°) [d] calc. [c]
1*R* (A, Ni1**)**	Λ	10.0(1)	10.8 Λ	20.6(1)	21.8(10)	25.3 Λ
1*R* (B, Ni2**)**	(Λ)	1.80(9)		5.1(1)	16.1(1)	
1*S* (A, Ni1**)**	Δ	9.98(9)	10.8 Δ	20.8(1)	21.8(1)	25.3 Δ
1*S* (B, Ni2**)**	(Δ)	1.73(9)		5.28(8)	16.4(1)	

[a] The round brackets indicated a faint chirality at Ni.

[b] Dihedral angle θ between the two planes formed by the donor atoms with the metal atom (cf. Scheme 1), that is, N1–Ni–O1 and N2–Ni–O2 (molecule **A**) and respective numbering in molecule **B**.

[c] By DFT geometry optimizations at B3LYP/6-31G(d) level; the calculated chirality at Ni is also given.

[d] Folding angle defined as the angle between O-Ni-N and O-C-C-C-N (cf. Scheme 3) with all these atoms forming the six-membered $NiNOC_3$ chelate ring. Each chelate ring has a folding angle, hence, there are two independent folding angles in a molecule.

Different from our previous studies on four-coordinated Cu(II) with asymmetric (A^B) and chiral Schiff base ligands[12,42] the distortion from square-planar, as assessed by the dihedral angle θ (cf. Scheme 1b) at the Ni atoms in **1*R*** and **1*S*** has become very small. The dihedral angle θ is only 10° for molecules **A** and less than 2° for molecules **B**. The experimental angle of about 10° agrees well with the angle of 10.8° from a DFT geometry optimizations at B3LYP/6-31G(d) level for Λ-Ni-*R*-L1 (**1*R***) (see above). This difference in dihedral angle θ could explain the formation of the two independent molecules **A** and **B**. The two molecules **A** and **B**, after relaxation of the hydrogen atoms at B3LYP/6-31G(d) level, have different DFT energies, molecule **A** being more stable by 1.8 kcal/mol. This is similar to the difference found between fully optimized **Λ-** and **Δ-Ni-1*R*** structures described above.

Yet, the conformational difference between the two symmetry independent molecules **A** and **B** is better explained with the help of Scheme 3. Each Ni-naphthaldiminato half does not assume a planar arrangement. Instead, each six-membered $NiNOC_3$ chelate ring is folded "up-or-down" hinging on the N---O vector to assume an envelope conformation.[43] In each molecule **A** and **B**, the folding of the two chelate rings occurs to the same side of the $Ni\mathit{N_2O_2}$ plane. The folding angles ϕ, that is, the angles defined by the $Ni\mathit{N_2O_2}$ plane and each of the naphthaldiminato planes (Scheme 3), are listed in Table 4. The folding in molecule **A** with Ni1 is more pronounced with very similar folding angles of ϕ~21° than in molecule **B** with Ni2 which has smaller and two different folding angles of 5° and 16°. An overlay of both molecules in each structure illustrates the different folding direction (Figure 4). The folding angles measured for DFT-optimized structures are also listed in Table 4, and they agree well with the values measured for molecule **A** in the crystals.

The combination of the folding in the $NiNOC_3$ ring, the intrinsic curvature in the naphthaldiminato ligand, and the concurrence of these two phenomena for the two ligands, creates an overall complex conformation around the nickel atom which has a helical appearance. The helicity can be differentiated into right-handed (*P*) or left-handed (*M*) as shown in Scheme 3. With their different "up-or-down" folding the two symmetry-independent molecules **A** and **B** found in the crystal assume a different helicity. For example, in Ni-*R*-L1 (**1*R***) the molecule with Ni1 is *M*-helical, the molecule with Ni2 is *P*-helical, and vice versa in Ni-*S*-L1 (**1*S***) (Scheme 3). This *P*- or *M*-conformational helicity is in addition to the Λ- or Δ-metal-centred chirality. Noteworthy, the left-handed *M*-conformation with the large folding angle ϕ of about 21° goes together with the more distinct dihedral angle θ of 10° for the clearly Λ-chiral molecule **A** in **1*R*** (and conversely right-handed *P* with the clearly Δ-chiral molecule **A** in **1*S***). Whereas the right-handed *P*-conformation with the smaller and uneven folding angles ϕ of 5° and 16°combine with the barely recognizable Λ-chiral molecule **B** in **1*R*** which has only a very small dihedral angle $\theta < 2°$, that is, essentially square planar (and the other way around *M* with the barely recognizable Δ-chiral molecule **B** in **1*S***) (see Scheme 3). The two angles θ and ϕ, describing together the deviation from an ideal square planar metal geometry with all-planar naphthaldiminato ligands, appear to be correlated with each other. The essentially square-planar Ni configuration in the **B** molecules in **1*R*** and **1*S*** may be seen as an effort of the *P*- (in **1*R***) and *M*-configuration (in **1*S***) to invert the Ni configuration. Evidently *P* prefers to have Δ at Ni and *M* to have Λ. This is confirmed by DFT results and by CD spectroscopy. Our DFT structures (see Electronic Spectra section and Table 4) show a strong prevalence for the Δ(Ni)/*P* (or Λ(Ni)/*M*) combination. The DFT lowest energy structure has large dihedral θ and folding ϕ angles, with absolute values very similar to those measured for molecule **A**. In turn, solution CD spectra and CD calculations give clear evidence that the Λ- (in **1*R***) and Δ-configuration (in **1*S***) is mostly retained (although it could partly invert upon conformational rearrangement).[14,41] Further studies are necessary to detect and quantify any inversion phenomenon occurring in solution. Possibly, the *P*- and *M*-conformational helicities may invert dynamically in solution akin to a bird's flap with its wings, as sketched in Figure 5. The structure with an all-planar Ni(bis-naphthaldiminato) moiety (in the middle of Figure 5), though not necessarily coinciding with the real transition state, offers an estimate of the conversion barrier (around 3.5 kcal/mol) between *P*- and *M*-conformational isomers of compound ***1R***, allowing for a very fast process. Very likely, the unfavorable *P* (in **1*R***) and *M*-configuration (in **1*S***) in the crystals inverts upon dissolution. It should be noted that the chelate-ring folding, when idealized, keeps the C_2-symmetry of the molecule.

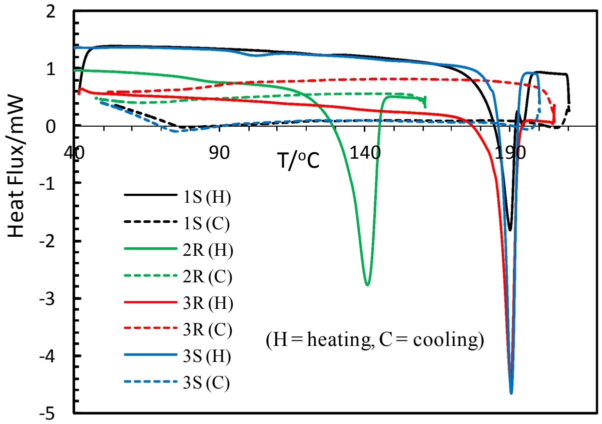


Figure 6. DSC analyzes curves of heating and cooling for the compounds.

Thermally induced structural phase transformation

Thermally induced structural phase transformation has been reported for transition metal-chiral *N*,*O*-chelates complexes, accompanying a change from distorted square planar/tetrahedral at the solid state to regular square planar/tetrahedral geometry at isotropic liquid phase.[8a-d,12,13,15,21,44,45,46] Differential Scanning Calorimetry (DSC) has successfully been used to study the phenomenon. Thus DSC heating curves of the present compounds show an exothermic peak at *ca.* 190 °C for **1*S***, **3*R***, **3*S*** and 141 °C for **2*R*** (Figure 6 and Table 5), while cooling curves show no corresponding peak on the reverse direction. The results demonstrate a thermally induced irreversible phase transformation as reported for the analogous Ni(II)-*N*,*O*-chelate complexes.[8c-d,13]

Table 5. Thermally induced structural phase transformation data for the compounds.

Compunds (physical appearence)	Peaks (T/°C)	ΔH (kJ mol^{-1})
1*S* (dark brown block shaped crystal)	190.1^{a}	−33.01
2*R* (greenish microcrystals)	140.8	−28.03
3*R* (greenish microcrystals)	190.2	−36.34
3*S* (greenish microcrystals)	190.7	−42.62

^{a} Reported value is 183°C for the analogous [(*R*)-N-1-(phenyl)ethyl-X-salicylaldiminato]Ni(II).**Error! Bookmark ot defined.**d

Cyclic voltammetry

Cyclic voltammograms (CV) of the free Schiff base (*S*-HL1) and compounds **1*S*** and **3*R*** were recorded at the range of −0.50 to 1.50 V *versus* Ag/AgCl in acetonitrile using different switching potentials at varying scan rates, respectively (Figure 7 and Supporting Information). The free Schiff base solution shows three anodic waves at *ca.* E_{a1} = 0.73, E_{a2} = 1.00 and E_{a3} = 1.20V (Figure 7a). Among them the former two waves are also common in the electrolyte (TBAP) solution (Figure 7a, dashed line), which shows corresponding reduction waves at *ca.* E_{c1} = 0.70 and E_{c2} = 0.90 V. Hence, the latter wave (E_{a3}) is due to the oxidation of the free Schiff base ligand. Voltammograms of **1*S***, **2*R*** and **3*R*** (Figure 7b and Supporting Information) are identical and show an additional anodic wave at *ca.*1.30 V (E_{a4}), which becomes more significant at higher scan rate, and is associated with the oxidation wave for the $[Ni(L)_2]/[Ni(L)_2]^+$ couple.[47,48] However, the corresponding cathodic wave is not detected even at higher scan rates, because of the instability of the cationic species ($[Ni(L)_2]^+$) which undergo a rapid irreversible reaction to produce an electrode-inactive species.[47a] The voltammograms in the cathodic region (i.e., 0 to −0.50 V) show a reduction wave at *ca.* −0.35 V (E_c) for $[Ni(L)_2]/[Ni(L)_2]^-$ couple (Figure 7b and Supporting Information), which overlaps with the decomposition peak of the electrolyte (TBAP) at higher scan rates.[48a] In fact, a corresponding poor oxidation wave is seen in the reverse scan, which undergoes rapid chemical transformation due to instability of the $[Ni(L)_2]^-$ species. Analysis of voltammograms at varying scan rates (0.02 to 0.40 V/s) demonstrates a linear relationship between the anodic peak current (I_a) at *ca.*1.30 V and the square root of the scan rate ($\nu^{1/2}$, Figure 8), indicating a diffusion-controlled electrochemical process.

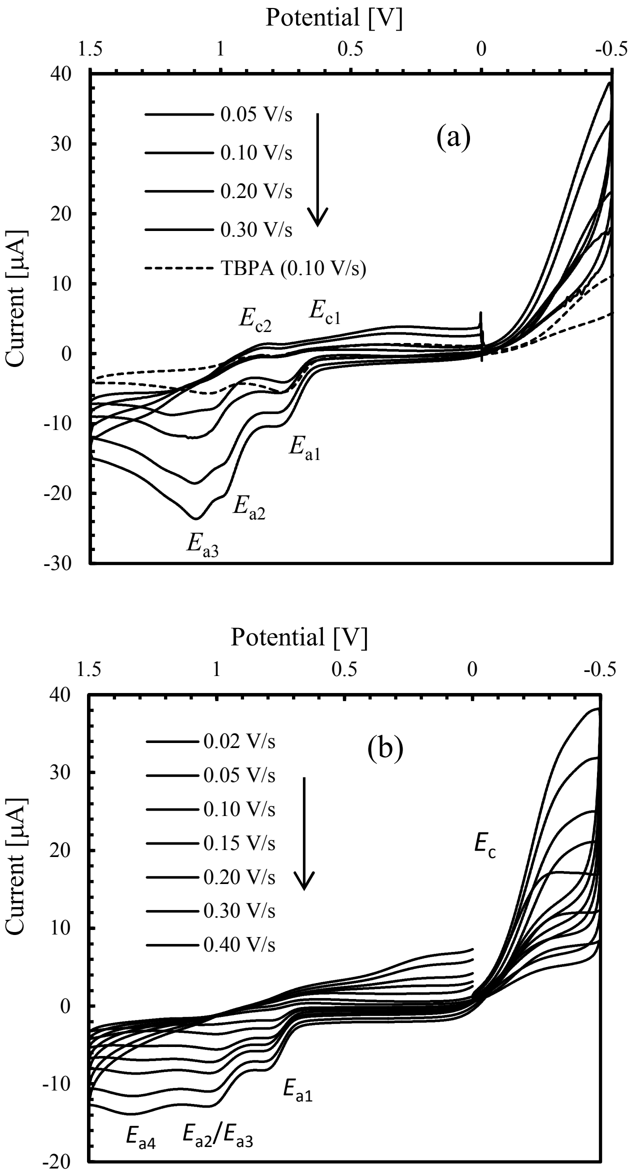


Figure 7. Cyclic voltammograms of (a) *S*-HL1 (1.5 mmol/L) and (b) **1*S*** (1.0 mmol/L); TBAP (0.1 mol/L) at varying scan rates in acetonitrile at 25 °C.

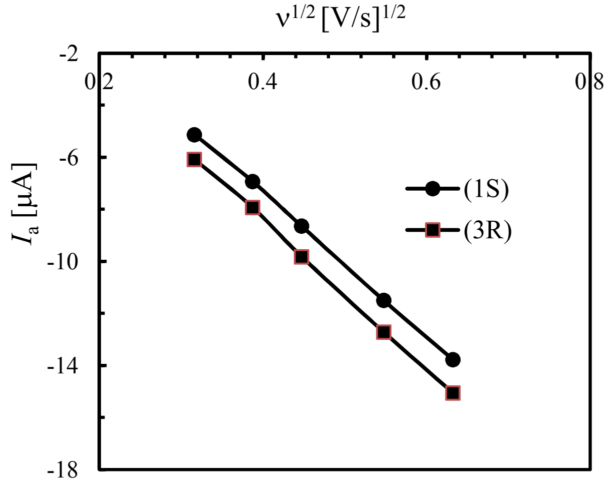


Figure 8. Change of anodic current (I_a) at *ca.*1.30 V *vs.* square root of the scan rate, ($\nu^{1/2}$).

Conclusions

We have reported the synthesis, characterization, X-ray structure, and molecular modeling study of a series of chiral *bis*(naphthaldiminato)Ni(II) complexes **1-3** with distorted square planar geometry around the metal ion. These complexes show a remarkable stereochemistry because the ligand configuration is selectively and concurrently transferred to the metal chirality and to the conformational helicity of the ligands. Thus, a ligand with *R* configuration favors the formation of a complex with Λ chirality at Ni and *M* ligand helicity. The stereochemical behavior of our series of complexes may be of interest in different fields based on the multiplication and amplification of chirality. First, the chiral folding of the naphthaldiminato moieties imparts the complexes a discrete helicity which may be the starting point to obtain supramolecular helicates in a very selective and efficient way.[5] Second, the complexes are possibly expected to induce high twisting powers when used as dopants for cholesteric liquid crystals.[49]

Experimental section

IR-spectra were recorded on a Nicolet iS10 spectrometer as KBr disc at ambient temperature. UV-Vis. spectra were obtained with Shimadzu UV 1800 spectrophotometer in cyclohexane at 25 °C. Elemental analyses were done on a Vario EL instrument from Elementaranalysensysteme. An Epsilon™ Instruments (BASi) electrochemical analyzer was used for cyclic voltammetry (CV) experiment containing tetra-N-butyl-ammonium-hexaflorophosphate (TBAP) as supporting electrolyte in acetonitrile at 25 °C. The three-electrode measurement was carried out with a platinum disc working electrode, a platinum wire auxiliary electrode and Ag/AgCl reference electrode. The solution containing the compounds and TBAP was deoxygenated for 10 minutes by passing nitrogen gas prior to run the experiments. CD spectra were obtained with JASCO Spectropolarimeter (J715) in cyclohexane on 2-2.5 mM samples. For each solution sample, three distinct spectra were recorded using cells with different path-length (0.1 mm, 5 mm and 10 mm) to cover the whole spectral range from 190-200 to 900 nm by keeping the absorbance below 1.5 AU. direction and by flipping the disc with respect to the vertical, to check the presence of artifacts. H-NMR spectra were run on a Bruker Avance DPX 400 Spectrometer (operating at 400 MHz, ^{1}H)in $CDCl_3$ (δ7.25 ppm) at 20 °C. EI-MS: Thermo-Finnigan TSQ 700. Isotopic distribution patterns for $^{58/60}$Ni (in **1*R*/*S*** and **2*R*/*S***) or combined $^{63/65}$Ni+$^{79/81}$Br (in **3*R*/*S***) containing ions are clearly visible in the mass spectra.

General procedure to synthesise the complexes

Two equivalents of enantiopure (*R* or *S*)-N-1-(C_6H_5)ethyl-2-oxo-1-naphthaldimine (*R* or *S*-HL1) (341mg, 1.24mmol) dissolved in 5mL methanol was added into 5mL hot methanolic solution of $Ni(O_2CCH_3)_2·4H_2O$ (154mg, 0.62mmol) and stirred the solution for 6-8h at room temperature. Color changes from light green to greenish brown in clear solution. Reduced the volume of solvent to *ca.*50%, and left standing this clear solution for crystallization *via* slow solvent evaporation of solvent at room temperature. Dark brown blocked shape crystals of Ni-*R*-L1 (**1*R***) or Ni-*S*-L1 (**1*S***), suitable for X-ray measurement, were obtained within 5-6d. The crystals were separated, washed with methanol (2x2mL), and dried in air for 3-4 d.The same procedure was followed for syntheses of Ni-*R*-L2 (**2*R***) or Ni-*S*-L2(**2*S***) using the Schiff bases of (*R* or *S*)-N-1-(*p*-OMeC_6H_4)ethyl-2-oxo-1-naphthaldimine (*R* or *S*-HL2), and obtained greenish microcrystals after 5-6 d, not suitable for X-ray measurement. For syntheses of Ni-*R*-L3 (**3*R***) or Ni-*S*-L3 (**3*S***) using (*R* or *S*)-N-1-(*p*-BrC_6H_4)ethyl-2-oxo-1-naphthaldimine (*R* or *S*-HL3), green precipitate was formed within 30 min. of stirring the solution. Continued to stirring for 6-8 h, and left standing this solution for 8-10h until complete precipitation. Filtered off, and washed the precipitate with methanol (2x2mL). Green microcrystals of Ni-*R*-L3 (**3*R***) or Ni-*S*-L3 (**3*S***) were obtained after drying the sample in air for 3-4 d.

Bis{(*R*)-N-1-(C_6H_5)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}nickel(II) (**Ni-*R*-L1**; **1*R***). Dark brown blocked shaped crystals. Yield 275mg (73%). – IR (KBr, cm^{-1}): ν = 3057, 3027, 2971w (H-C), 1617, 1605vs (C=N), and1541s (C=C). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (d, *J* = 6.5Hz, 6H, C*H*$_3$), 6.64 (d, *J* = 9.2Hz, 2H), 6.78 (t, *J* = 7.4Hz, 2H), 7.05 (d, *J* = 8.4Hz, 2H), 7.34 (d, *J* = 8.4Hz, 4H), 7.42 (t, *J* = 7.4Hz, 4H), 7.60 (m, 6H), 7.74 (d, *J* = 8.8Hz, 2H), and 11.05 (s, 2H, C*H*N). – ESI-MS: 607 (30) [*M*+H]$^+$, 331 (58) [*M*-HL1]$^+$, 228 (100) [$C_{10}H_6$(CHNH)(O)Ni] and 105 (33) [$CH(C_6H_5)(CH_3)$]$^+$. – $C_{38}H_{32}N_2O_2Ni$ (607.40): calcd. C 75.14, H 5.31, N 4.61; found C 75.35, H 5.04, N 4.36.

Bis{(*S*)-N-1-(C_6H_5)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}nickel(II) (**Ni-*S*-L1**; **1*S***). Dark brown blocked shaped crystals. Yield 260 mg (67%). – IR (KBr, cm^{-1}): ν = 3055, 3032, 2970w (H-C), 1616, 1605vs (C=N), and 1540s (C=C). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (d, *J* = 6.5Hz, 6H, C*H*$_3$), 6.62 (d, *J* = 9.2Hz, 2H), 6.76 (t, *J* = 7.4Hz, 2H), 7.05 (d, *J* = 8.4Hz, 2H), 7.32 (d, *J* = 8.4Hz, 4H), 7.41 (t, *J* = 7.4Hz, 4H), 7.59 (m, 6H), 7.72 (d, *J* = 8.8Hz, 2H), and 11.02 (br, 2H). – ESI-MS: 607 (20) [*M*+H]$^+$, 331 (45) [*M*-HL1]$^+$, 228 (100) [$C_{10}H_6$(CHNH)(O)Ni] and 105 (25) [$CH(C_6H_5)(CH_3)$]$^+$. – $C_{38}H_{32}N_2O_2Ni{\cdot}H_2O$ (625.41): calcd. C 72.98, H 5.48, N 4.48; found C 71.46, H 4.86, N 4.34.

Bis{(*R*)-N-1-(*p*-OMeC_6H_4)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}nickel(II) (**Ni-*R*-L2; 2*R***). Greenish microcrystals. Yield 300mg (72%). – IR (KBr, cm^{-1}): ν = 3052, 3043w (H-Ar), 1624, 1605vs (C=N), and 1541s (C=C). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (d, *J* = 6.5Hz, 6H, C*H*$_3$), 3.83 (s, 6H, OC*H*$_3$), 6.56 (d, *J* = 7.2Hz, 2H), 6.96 (m, 6H), 7.09 (d, *J* = 8.4Hz, 2H), 7.36 (d, *J* = 8.4Hz, 2H), 7.56 (d, *J* = 7.4Hz, 4H), 7.61 (d, *J* = 8.4Hz, 2H), 7.88 (d, *J* = 8.8Hz, 2H), and 12.81 (br, 2H). – ESI-MS: 667 (15) [*M*+H]$^+$, 306 (10) [HL2+H]$^+$, 135 (100) [$CH(CH_3)(C_6H_4OCH_3)$]$^+$ and 105 (15) [$CH(C_6H_5)(CH_3)$]$^+$. – $C_{40}H_{36}N_2O_4Ni$ (667.45): calcd. C 71.98, H 5.44, N 4.20; found C 71.32, H 5.29, N 4.12.

Bis{(*S*)-N-1-(*p*-OMeC_6H_4)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}nickel(II) (**Ni-*S*-L2; 2*S***). Greenish microcrystals: Yield 280 mg (68%). – IR (KBr, cm^{-1}): ν = 3050, 3025w (H-Ar), 1642, 1611vs (C=N), and 1541s (C=C). – ESI-MS: 667 (5) [*M*+H]$^+$, 306 (10) [HL2+H]$^+$, 135 (100) [$CH(CH_3)(C_6H_4OCH_3)$]$^+$ and 105 (20) [$CH(C_6H_5)(CH_3)$]$^+$. – $C_{40}H_{36}N_2O_4Ni$ (667.45):

calcd. C 71.98, H 5.44, N 4.20; found C 71.43, H 5.30, N 4.09.

Bis{(*R*)-N-1-(*p*-BrC_6H_4)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}nickel(II) (**Ni-*R*-L3; 3*R*):** Greenish microcrystal. Yield 360mg (72%). – IR (KBr, cm^{-1}): ν = 3051, 3027, 2973w (H-C), 1616, 1607vs (C=N), and1541s (C=C). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94 (d, *J* = 6.0Hz, 6H, C*H*$_3$), 6.63 (d, *J* = 8.8Hz, 2H), 6.88 (d, *J* = 7.2Hz, 2H), 7.12 (t, *J* = 6.8Hz, 2H), 7.37 (d, *J* = 7.4Hz, 4H), 7.55 (d, *J* = 8.4Hz, 6H), 7.67 (d, *J* = 7.0Hz, 2H), 7.82 (d, *J* = 8.4Hz, 2H), and 11.27 (br, 2H). – $C_{38}H_{30}N_2O_2Br_2Ni{\cdot}2H_2O$ (801.24): calcd. C 56.96, H 4.28, N 3.50; found C 56.24, H 3.86, N 3.40.

Bis{(*S*)-N-1-(*p*-BrC_6H_4)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}nickel(II) (**Ni-*S*-L3**; **3*S***). Greenish microcrystals. Yield 350 mg (70%). – IR (KBr, cm^{-1}): ν = 3057, 3030, 2972w (H-C), 1616, 1605vs (C=N), and 1541s (C=C). – EI-MS (70 eV): *m*/*z* (%) = 764 (10) [*M*]$^+$, 411 (100) [*M*-HL3]$^+$, 353 (30) [HL3]$^+$, 229 (20) $[C_{10}H_6(O)(CHNH)Ni+H]^+$, 183 (35) $[C_6H_4(Br)(CHCH_3)]^+$, 170 (60) $[C_{10}H_6(O)(CHNH)]^+$, and 104 (60) $[CH_3CHC_6H_5\text{-}H]^+$ (isotopic distribution pattern resulting from combination of $^{58/60}$Ni+$^{79/81}$Br containing ions are clearly visible following the peaks at 764, 411, 229 while for $^{79/81}$Br containing ions at 353, and 183). – $C_{38}H_{30}N_2O_2Br_2Ni{\cdot}2H_2O$ (801.24): calcd. C 56.96, H 4.28, N 3.50;found C 56.04, H 3.66, N 3.42).

X-ray crystallography

Single-crystals of enantiomeric pair **Ni-*R*-L1** (**1*R***) and **Ni-*S*-L1** (**1*S***) were carefully selected under a polarizing microscope and mounted on a loop. *Data collection*: Bruker APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 203(2) K; *ω*-scans (see Table 6). Data collection and cell refinement with APEX2,[50] data reduction with SAINT (Bruker).[51] *Structure analysis and refinement:* The structures were solved by direct methods (SHELXS-97),[52] refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite,[51] empirical (multi-scan) absorption correction with SADABS (Bruker).[53] All non-hydrogen positions were refined with anisotropic temperature factors. Hydrogen atoms for aromatic CH, aliphatic or olefinic CH, CH_2 and OH groups were positioned geometrically (C–H = 0.94 Å for aromatic CH, C–H = 0.94 Å for olefinic CH, 0.99 for aliphatic CH and 0.97 Å for CH_3,) and refined using a riding model (AFIX 43 for aromatic CH, AFIX 13 for aliphatic CH, AFIX 137 for CH_3), with $U_{iso}(H) = 1.2U_{eq}(CH, CH_2)$ and $U_{iso}(H) = 1.5U_{eq}(CH_3)$. Details of the X-ray structure determinations and refinements are provided in Table 6. Graphics were drawn with DIAMOND (Version 3.2).[38] Computations on the supramolecular interactions were carried out with PLATON for Windows.[41] The structural data for this paper has been deposited with the Cambridge Crystallographic Data Center (CCDC-numbers 1405162-1405163). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Computational section

Conformational searches and geometry optimizations were run with Spartan'14 (Wave function, Inc. Irvine, CA). Excited-state CD calculations were run with Gaussian09.[50] Initial structures were generated starting from the available X-ray structure of **Λ-Ni-1*R***complex. An initial structure with opposite configuration at the metal, **Δ-Ni-1*R***, was obtained by mirror inversion of the whole complex, followed by manual inversion of the carbon chirality centers only. Conformational searches were run with molecular mechanics, using the Molecular Merck force field (MMFF). The geometry around the metal was kept fixed by constraining the O-Ni and N-Ni bond lengths and the O-Ni-O and N-Ni-N bond angles at their respective X-ray values. All the remaining rotatable bonds were included in the conformational search (i.e., varied systematically) and optimized with MMFF. All structures thus obtained were fully re-optimized with DFT using B3LYP functional and 6-31G(d) basis set on all atoms.[51] Excited state calculations were run with the TDDFT method. A preliminary set of calculations was run to test the performance of various DFT functionals and basis sets, including a limited number of excited states (roots). The following functionals were tested: B3LYP, CAM-B3LYP, M06, PBE1PBE, wB97X-D and the two basis sets SVP and TZVP.[50] Final calculations including 80 roots were run with the B3LYP/TZVP combination. The spectra were generated using the program SpecDis[52] by applying a Gaussian band shape with 0.2 eV exponential half-width. Rotational strengths calculated with the dipole-length gauge were employed, the differences with dipole-velocity values being negligible for most transitions.

Table 6. Crystal data and structure refinement for the compounds.

.	**Ni-*R*-L1 (1*R*)**	**Ni-*S*-L1 (1*S*)**
Empirical formula	$C_{38}H_{32}N_2O_2Ni$	$C_{38}H_{32}N_2O_2Ni$
M / g mol^{-1}	607.37	607.37
Crystal size / mm^3	0.072 x 0.072 x 0.067	0.56 × 0.36 × 0.11
Temperature / K	95	100
θ range / °(completeness)	1.97-27.50 (99.8%)	1.66-25.23 (99.1%)
h; k; l range	–8,12; –15, 19; ±26	±11; ±18; ±24
Crystal system	monoclinic	monoclinic
Space group	$P\,2_1$ (no. 4)	$P\,2_1$ (no. 4)
a /Å	9.5282(16)	9.5328(9)
b /Å	15.355(3)	15.2970(16)
c /Å	20.655(4)	20.560(2)
β /°	90.146(7)	90.192(6)
V /Å^3	3021.93(10)	2998.1(5)
Z/ D_{calc}(g cm^{-3})	4/1.335	4/1.346
μ (Mo Kα) / mm^{-1}	0.679	0.685
F(000)	1272	1272
Max./min. transmission	0.956/0.953	0.700/0.928
Reflections collected	28227	25081
Independent reflect. (R_{int})	12217 (0.0617)	10664 (0.0573)
Data / restraints / parameters	12217 / 13 / 779	10664/1/779
Max. / min. $\Delta\rho$ / e.Å$^{-3\ a}$	0.688/ -0.948	0.394/-0.661
$R1/wR2$ [I> 2σ(I)] ^{b}	0.0494/ 0.0944	0.0384/0.0922
$R1/wR2$ (all data) ^{b}	0.0678/ 0.1016	0.0438/0.0945
Goodness-of-fit on F^{2c}	0.991	1.006
Flack parameter ^{d}	0.008(10)	0.040(8)

[a] Largest difference peak and hole. – $^bR_1 = [\Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|]$; $wR_2 = [\Sigma\,[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. – [c] Goodness-of-fit = $[\Sigma\,[w(F_o^2-F_c^2)^2]\,/(n-p)]^{1/2}$. – [d] Absolute structure parameter.[25]

Acknowledgements

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† Electronic Supplementary Information (ESI†) available: ESI-MS data, ^{1}H-NMR spectra and data, Cyclic voltammograms, Analysis of supramolecular interactions, and CIF files reported in this paper. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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