Chirality and diastereoselection of $\Delta/\Lambda$-configured tetrahedral zinc(II) complexes with enantiopure or racemic Schiff base ligands

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1. Introduction

Syntheses, spectroscopy, stereoselectivity, and crystal structures of chiral transition metal-complexes are of continued interest [1–3] including the complexes of chiral salicylaldimine or chiral alkoxy-salicylaldiminato Schiff base ligands [4–9]. Optically active Schiff base ligands and their transition metal-complexes have been synthesized and used successfully as potential chiral catalysts [8–13]. Tetrahedral or pseudo-tetrahedral metal-complex containing two asymmetric N=O chelate ligands affords $C_2$-symmetric $\Delta$- and $\Lambda$-configurations at the metal centre [5,6,14]. The use of enantiopure R- or S-N=O chelate ligands leads to the formation of diastereomers $\Delta$-M-R-N=O and $\Lambda$-M-R-N=O or $\Delta$-M-S-N=O and $\Lambda$-M-S-N=O, whereas racemic R/S-N=O gives all these four diastereomers (cf. Scheme 1 and 2). However, due to intramolecular non-covalent interactions within the metal-chiral chelate complexes there is a free-energy difference between the diastereomers, and one diastereomer can be predominantly formed. Such diastereoselection has been reported in tetrahedral or pseudo-tetrahedral [M(R- or S-N=O)2] (M = Co, Cu, Ni, Zn) with the predominant formation of $\Delta$- or $\Lambda$-configured diastereomer as evidenced by the X-ray studies in the solid state and by the circular dichroism (CD) pattern at the azomethine $\pi \rightarrow \pi^*$ transitions of the coordinated ligands in solution [5,6]. Recently, it has been shown that the induced metal-centered $\Delta$- or $\Lambda$-chirality is correlated to the chirality of the bidentate enantiopure (R)-N=O or (S)-N=O ligands in pseudo-tetrahedral [Zn(R- or S-N=O)2] (R- or S-N=O = (R or S)-N-1-(4-X-phenyl)-salicylaldiminato) [14] (cf. Scheme 3). The R- or S-ligand chirality induced a $\Lambda$-M or $\Delta$-M configuration, respectively, in the solid state as deduced from the X-ray crystal studies. Further, the diastereoselection of [Zn(R- or S-N=O)2] were investigated in solution by $^1$H NMR and vibrational circular dichroism (VCD) spectroscopy. The appearance of two signals for the Schiff base imine proton in $^1$H NMR indicated an equilibrium of
both Δ- and Λ-diastereomers with a diastereomeric ratio of ca 20:80 (%) in [Zn(R''N''O)2].

In recent years we have investigated the transition metal-complexes with chiral base ligands, (R or S)-N-1-(4-X-phenyl) ethyl-salicylaldimine/naphthaldimine, (R or S), or R/S)-2-(2-hydroxy-1 or 2-phenylethylimino)methyl]phenol, (R)-, 2-(R, benzaldimine)-2-phenylethanol or with chiral amino acids/ alcohols [15–18]. In the present paper, we study the diastereoselection in the tetrahedral Δ/Λ- or Λ/Δ-bis[(S or R)-2-((2-hydroxy-1-phenylethylimino)methyl]phenoxide-κ²N,O]zinc(II), (Δ/Λ-Zn-S-L1, 1 or Λ/Δ-Zn-R-L1, 2) (Scheme 1), and Δ/Λ- and Λ/Δ-bis[(R/S)-2-((2-hydroxy-2-phenylethyl)-methyl]phenoxide-κ²N,O]zinc(II) (Δ/Λ- and Λ/Δ-Zn-R(S)-L2, 3) (Scheme 2). To the best of our knowledge, compound 3 is the first example of a structurally elucidated racemic mononuclear Zn(II)-chiral alkoxysalicylaldimine complex that provides diastereoselectivity.

2. Experimental

IR-spectra were recorded on Nicolet iS10 spectrometer as KBr disc at ambient temperature. UV–Vis. spectra were obtained with Shimadzu UV1800 spectrophotometer in C6H6, CHCl3, CH2Cl2, MeOH, DMF, DMSO, and THF at 25 °C. Polarimetric measurements were carried out with UniPol L instrument from Schmid + Haensch in CHCl3 at 25 °C. CD spectra were obtained with JASCO Spectropolarimeter (J715) in chloroform at 25 °C. 1H NMR spectra were recorded on a JEOL AC 300 spectrometer operating at 300 MHz (1H) at 20 °C with calibration against the residual protonated solvent signal of CDCl3. ESI-mass (positive) spectra were carried out on QStar Elite quadrupole time-of-flight (Q-TOF) instrument (MDS Analytical Technologies, Concord, ON, Canada), equipped with a “turbo ion spray” ion source. Mass spectra showed metal isotope pattern arising from the distribution of 65Zn (100%), 66Zn (57%), and 68Zn (38%), and peaks were given for the more abundant isotope. The enantiopure Schiff bases (S- or R-HL1) and racemic (R/S-HL2) were synthesized according to our previous literature [18a].

2.1. General procedure to synthesize the complexes

The Schiff base ligand, e.g. (S)-2-{[(E)-2-hydroxy-1-phenylethylimino]methyl]phenol (S-HL1) (122 mg, 0.51 mmol) was added to a solution of Zn(O2CCH3)2·2H2O (56 mg, 0.26 mmol) in methanol (10 mL) with stirring. A solution of NaHCO3 (41 mg, 0.50 mmol) in
methanol (5 mL) was poured into the reaction mixture, and stirring was continued at room temperature. After 48 h of stirring a light-yellow solution had formed. This solution was then left standing for crystallization via slow solvent evaporation at rt. Light orange-yellow micro crystals (not suitable for single-crystal X-ray diffraction) were precipitated out within 2 d. The crystals were separated by filtration, washed 3 times with methanol (2 mL) and diethyl ether (2 mL) in each. The crystals were dried in air for 3–4 d to give the product A/A-bis[S]-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenoxy-k’N,O[zo]zinc(II) (1). The same procedure was followed for the syntheses of compounds 2 and 3 using ligands R-HL1 and R/S-HL2, respectively.

2.1.1. A/A-bis[S]-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenoxy-k’N,O[zo]zinc(II), (A/A-Zn-S-L1)

Yield 95 mg (67%). $\delta^{1} J = + 226^\circ$ (c = 0.30 g/100 mL) at 589 nm in CHCl$_3$, IR (KBr, cm$^{-1}$): ~32500 (ν-H), 3070, 3052, 2955s (v C-H), 1621vs (v C=O), 1587s (v C=C). $\delta^{13}$ NMR (300 MHz, CDCl$_3$): $\delta = 3.98$ (m, 4H, CH$_2$), 4.05 (m, 2H, OH), 4.63-4.41 (m, 2H, CH), 6.67-6.83 (m, 4H, H$_2$A), 7.04-7.07 (m, 4H, H$_2$S), 7.32-7.43 (m, 10H, H-Ph), and 8.40-8.22 (s, 2H, CHN) [$\Lambda^{\prime}$/A-Zn-S-L1= 67/33 (%)]. The structure of this compound was solved by direct methods (SHELX-97) [22]; refinement was done by full-matrix least squares on $F^2$ using the SHELXL-97 program suite [22]; empirical (multi-scan) absorption correction was done with SADABS [23]. 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 = 0.93 Å for aromatic CH, C-H = 0.93 Å for aliphatic and olefinic CH, C-H = 0.97 Å for CH$_2$, O-H = 0.82 Å for OH) and refined using a riding model (AFIX 43 for aromatic CH, AFIX 13 for aliphatic CH, AFIX 23 for CH$_2$, AFIX 147 for OH), with $U_{iso}$(OH) = 1.2$U_{iso}$(CH, CH$_2$) and $U_{iso}$(H) = 1.5$U_{iso}$(OH). Details of the X-ray structure determinations and refinements are provided in Table 1. Graphics were drawn with DIAMOND (Version 3.2) [24]. Computations on the supramolecular interactions were carried out with PLATON for Windows [25].


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3. Results and discussion

Enantiopure (S or R)-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenol (S- or R-HL1) reacts with zinc(II)acetate in the presence of sodium bicarbonate to a mixture of the diastereomers A- and A-bis[S]-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenoxy-k’N,O[zo]zinc(II) (A/A-Zn-S-L1, 1) or A- and A-bis[R]-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}phenoxy-k’N,O[zo]zinc(II) (A/A-Zn-R-L1, 2), respectively (Scheme 1). Similarly, racemic (R/S)-2-{(E)-(2-hydroxy-1-phenylethylimino)methyl}

**Table 1**

<table>
<thead>
<tr>
<th>Crystal data and structure refinement for compound 3.</th>
<th></th>
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<tr>
<td><strong>Empirical formula</strong></td>
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<td><strong>M (g mol$^{-1}$)</strong></td>
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<tr>
<td><strong>Crystal size (mm$^{3}$)</strong></td>
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<tr>
<td><strong>Space group</strong></td>
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<tr>
<td><strong>µ (Mo Kα) (mm$^{-1}$)</strong></td>
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<td><strong>Reflections collected</strong></td>
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<td>763 (0.032)</td>
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<tr>
<td><strong>Max/min. transmission</strong></td>
<td>1169</td>
</tr>
<tr>
<td><strong>Reflected independent (Rint)</strong></td>
<td>0.548/0.749</td>
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<tr>
<td><strong>Reflections collected</strong></td>
<td>2989</td>
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<tr>
<td><strong>Independent reflection (Rint)</strong></td>
<td>763 (0.032)</td>
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<tr>
<td><strong>Data/restraints/parameters</strong></td>
<td>1169</td>
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<tr>
<td><strong>Max/min. transmission</strong></td>
<td>0.201/0.102</td>
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<tr>
<td><strong>Goodness-of-fit (GOF) on F$^{2}$</strong></td>
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<tr>
<td><strong>Flash parameter</strong></td>
<td>0.0303/0.0641</td>
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<tr>
<td><strong>Absolute structure parameter</strong></td>
<td>0.0617</td>
</tr>
</tbody>
</table>

*a* Largest difference peak and hole.

*b* $R_{1} = \sum||F_{o}|-|F_{c}||/\sum|F_{o}|$; $wR_{2} = \sum[w(|F_{o}|-|F_{c}|)^{2}] \sum[w(F_{o}^{2})]^{1/2}$.

*c* Goodness-of-fit is $\sum[w(F_{o}^{2} - F_{c}^{2})]^{2}/(n-p)$.$^{1/2}$.

*d* Absolute structure parameter [26].

Single crystals suitable for X-ray diffraction were grown by slow evaporation of solvent from a concentrated complex solution in hot methanol over 6–7 d at room temperature. A single-crystal of 3 was carefully selected under a polarizing microscope and mounted on a loop and all geometric and intensity data were taken from this sample using a Bruker Kappa APEX II CCD diffractometer with microfocus tube and graphite-monochromated Cu Kα radiation ($\lambda = 1.54178$ Å) at 23 ± 2 K; o- and o-scan. Data collection and cell refinement with APEX2 [20] data reduction with SAINT (Bruker) [21]. Structure analysis and refinement: The structure of 3 was solved by direct methods (SHELX-97) [22]; refinement was done by full-matrix least squares on $F^2$ using the SHELXL-97 program suite [22]; empirical (multi-scan) absorption correction with SADABS [23]. 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 = 0.93 Å for aromatic CH, C-H = 0.93 Å for aliphatic and olefinic CH, C-H = 0.97 Å for CH$_{2}$, O-H = 0.82 Å for OH) and refined using a riding model (AFIX 43 for aromatic CH, AFIX 13 for aliphatic CH, AFIX 23 for CH$_{2}$, AFIX 147 for OH), with $U_{iso}$(OH) = 1.2$U_{iso}$(CH, CH$_{2}$) and $U_{iso}$(H) = 1.5$U_{iso}$(OH). Details of the X-ray structure determinations and refinements are provided in Table 1. Graphics were drawn with DIAMOND (Version 3.2) [24]. Computations on the supramolecular interactions were carried out with PLATON for Windows [25].

2.2. X-ray crystallography

Single crystals suitable for X-ray diffraction were grown by slow evaporation of solvent from a concentrated complex solution in

\[L1 = \frac{1}{2} (33/67) \text{,} \]

3.1. Spectroscopy and analyses

ESI mass spectra show the parent ion peaks at m/z = 545/567 ([M+H/Na]+) for all the complexes, and the base peaks at 242/264 ([HL1 or HL2+H/Na]+) for the free Schiff bases. The infrared spectra of the zinc(II) complexes feature a very strong band at 1621–1645 cm⁻¹ for ν(C=N), and a shoulder (to the water peak) at ~3250 cm⁻¹ due to ν(CO–H), which is different from the strong broad band at 3200–3340 cm⁻¹ in the free Schiff base ligands [18]. Polarimetric measurements show the rotation to the right

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Electronic spectral data of Schiff bases and complexes in different solvents at 25 °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entity¹</td>
<td>Solvent</td>
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<tr>
<td>(S-HL1) (4.50 × 10⁻⁴)</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>(R-HL1) (4.50 × 10⁻⁴)</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>(R/S)-HL2 (4.15 × 10⁻⁴)</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>1 (1.47 × 10⁻⁴)</td>
<td>CHCl₃</td>
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<tr>
<td>1 (1.47 × 10⁻⁴)</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>1 (1.45 × 10⁻⁴)</td>
<td>MeOH</td>
</tr>
<tr>
<td>2 (1.50 × 10⁻⁴)</td>
<td>C₆H₆</td>
</tr>
<tr>
<td>2 (1.29 × 10⁻⁴)</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>2 (1.72 × 10⁻⁴)</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>2 (1.29 × 10⁻⁴)</td>
<td>MeOH</td>
</tr>
<tr>
<td>2 (1.38 × 10⁻⁴)</td>
<td>DMF</td>
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<tr>
<td>2 (1.15 × 10⁻⁴)</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>2 (2.41 × 10⁻⁴)</td>
<td>DMF</td>
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<tr>
<td>2 (1.72 × 10⁻⁴)</td>
<td>THF</td>
</tr>
<tr>
<td>3 (1.54 × 10⁻⁴)</td>
<td>C₆H₆</td>
</tr>
<tr>
<td>3 (1.93 × 10⁻⁴)</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>3 (2.29 × 10⁻⁴)</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>3 (1.90 × 10⁻⁴)</td>
<td>MeOH</td>
</tr>
<tr>
<td>3 (1.64 × 10⁻⁴)</td>
<td>DMF</td>
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<tr>
<td>3 (1.54 × 10⁻⁴)</td>
<td>DMF</td>
</tr>
<tr>
<td>3 (1.85 × 10⁻⁴)</td>
<td>THF</td>
</tr>
</tbody>
</table>

¹ Concentration in mol dm⁻³.

² λ in nm and ε in mol⁻¹ cm⁻¹; sh = shoulder.

Fig. 1. Electronic spectra of compounds 1 (A), 2 (B), and 3 (C) in different solvents and corresponding Schiff bases in CHCl₃ at 25 °C.

Fig. 2A. Electronic spectra of compound 2 with or without free ligand (R-HL1) in cyclohexane at 25 °C.

Fig. 2B. Electronic spectra of compound 2 (1.15 × 10⁻⁴ mol dm⁻³) in water at different time at 25 °C.
Electronic spectra of the Schiff base ligands and complexes (Fig. 1, Table 2) show a strong band/shoulder at the range of 300–350 nm with absorption maxima $\lambda_{\text{max}} = 316–326$ nm ($c = 2800–11000$ dm$^{-3}$ cm$^{-1}$) due to the intra-ligand $\pi \rightarrow \pi^*$ transitions for the imine group.[4–6,14–18]. There are also a very strong band below 300 nm due to the intra-ligand $\pi \rightarrow \pi^*$ transitions. This result strongly suggests no free ligand in the sample as shown in the CD spectral data of the complexes and Schiff base ligands in CHCl$_3$ at 25°C.

To check for the presence of free ligand in the sample, an electronic spectrum of compound 2 was taken in cyclohexane (Fig. 2A), in which 2 is insoluble but the ligand is well soluble, and the spectrum shows no band. Addition of a little amount of ligand (R-HL1) into this solution shows strong bands with $\lambda_{\text{max}} = 257/321$ nm for intra-ligand $n \rightarrow \pi^*$ and MLCT transitions, respectively with time dependent molar absorptivities ($\varepsilon$) ratio in DMSO (Fig. 1C). However, the spectra of the complexes in THF or DMSO are almost identical to those of the free Schiff base ligands (Fig. 1), strongly suggest the dissociation of the complexes.

For the related $\Delta$-bis[(R- or S)-N-(4-X-phenyl)ethyl-salicylaldiminato-$\kappa^2$N,O]zinc(II) complexes in reference [14] exhibit a $-\Delta/+\Delta$ pattern from longer to shorter wavelengths for the $\Delta$-Zn-R-L complexes together with negative optical rotation values (between $-164$ and $-228^\circ$ depending on X). It is probable that the CD signals originate rather from exciton coupling than from the chirality of the ligand. Based on the X-ray and VCD supported assignment for the very similar compounds in reference [14], complex 1 can be assigned to $\Delta$-Zn-S-L1, and complex 2 can be assigned to $\Lambda$-Zn-R-L1 as the major diastereomer.

**Table 3**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Assignments</th>
<th>$\lambda_{\text{max}}$ ($\Delta \varepsilon$)$^e$</th>
<th>ML excitation coupling: $\lambda_{\text{max}}$ ($\Delta \varepsilon$)$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S-HL1) ($1.33 \times 10^{-3}$)$^d$</td>
<td>$n \rightarrow \pi^<em>, \pi \rightarrow \pi^</em>$ transitions: $\lambda_{\text{max}}$ ($\Delta \varepsilon$)$^e$</td>
<td>&lt;300, 341 (+1.63)</td>
<td></td>
</tr>
<tr>
<td>(R-HL1) ($1.45 \times 10^{-3}$)$^d$</td>
<td></td>
<td>&lt;300, 341 (−1.14)</td>
<td></td>
</tr>
<tr>
<td>1 ($1.18 \times 10^{-3}$)</td>
<td>275 (−3.37), 321 (+3.08)</td>
<td>−</td>
<td>368 (+1.43)</td>
</tr>
<tr>
<td>2 ($1.17 \times 10^{-3}$)</td>
<td>278 (+5.33), 327 (−4.40)</td>
<td></td>
<td>391 (−1.28)</td>
</tr>
</tbody>
</table>

$^a$ Concentration in mol dm$^{-3}$.
$^b$ Data reproduced from ref. 18a.
$^c$ $\lambda$ in nm and $\Delta \varepsilon$ in mol$^{-1}$ dm$^3$ cm$^{-1}$.
$^d$ $\lambda_{\text{max}}$ in nm.

Electronic circular dichroism (ECD) spectra of 1, 2 and ligands S-HL1, R-HL1 (Fig. 3A, Table 3) show the expected mirror image relationship for the enantiomers, respectively in chloroform. Spectra show the bands with positive maxima at <300, 341 nm ($\Delta \varepsilon_{\text{max}} = +1.63$ mol$^{-1}$ dm$^3$ cm$^{-1}$) in S-HL1 and negative maxima at <300, 341 nm ($\Delta \varepsilon_{\text{max}} = −1.14$ mol$^{-1}$ dm$^3$ cm$^{-1}$) in R-HL1 for the intra-ligand $n \rightarrow \pi^*$ transitions, respectively. These bands are found in the complexes below 350 nm with maxima at 274 nm (−3.37), 321 nm (+3.08) in 1 and 278 nm (+3.33), 327 nm (−4.40) in 2, respectively. The spectra of the complexes further show the bands with maxima at 385 nm (+5.36) in 1 and 368 nm (+1.43), 391 nm (−1.28) in 2 for MLCT exciton coupling.

The electronic absorption (UV) spectra of 1 and 2 in chloroform (Fig. 3B) are not exactly identical and show a ratio of molar absorptivities ($\varepsilon$) of $n \rightarrow \pi^*$ (at 325 nm)/MLCT (at 365 nm) transitions to 0.9 and 1.2, respectively. This is due to the time-dependent loss of diastereomeric purity of 1 or 2 in solution. This change in diastereomeric mixtures is reflected in the partial non-mirror image relation of the MLCT exciton coupling between 360–400 nm (while $n \rightarrow \pi^*/\pi \rightarrow \pi^*$ bands are fully mirror image) for the complexes enantiomers (Fig. 3A). The time-dependent loss of diastereomeric purity of compound 3 in chloroform is shown in detail in $^1$H NMR studies below.

The CD spectra for the related $\Delta$-bis[(R- or S)-N-(4-X-phenyl)ethyl-salicylaldiminato-$\kappa^2$N,O]zinc(II) complexes in reference [14] exhibit a $-\Delta/+\Delta$ pattern from longer to shorter wavelengths for the $\Delta$-Zn-R-L complexes together with negative optical rotation values (between $-164$ and $-228^\circ$ depending on X). It is probable that the CD signals originate rather from exciton coupling than from the chirality of the ligand. Based on the X-ray and VCD supported assignment for the very similar compounds in reference [14], complex 1 can be assigned to $\Delta$-Zn-S-L1, and complex 2 can be assigned to $\Lambda$-Zn-R-L1 as the major diastereomer.

$^1$H NMR spectra of Schiff base ligands (Fig. 4) show the methylene and methine protons as doublet and triplet at $\delta = 3.98$ or 4.00 ($J = 6.6$ Hz) and 4.62 or 4.72 ppm ($J = 6.6$ Hz), respectively.
in S-HL1 or R-HL1. While, the methylene protons show two sets of
doublets of doublet-doublets at $\delta$ 3.75 and 3.96 ppm ($J = 8.0$, 7.2 Hz, $J = 0.6$ Hz), and the methine proton shows a doublet of
doublet at $\delta$ 5.06 ($J = 7.8$ Hz, $J = 4.0$ Hz) in R/S-HL2. The imine proton shows a sharp singlet at $\delta$ 8.60 (S-HL1), 8.54 (R-HL1), and 8.40 (R/S-HL2) ppm. The phenolic and alcoholic protons could not be
seen separately in the Schiff base ligands as in complexes.
The percentage of diastereomers is calculated from integration values of the Schiff base
imine proton signal [14]. The assignment of the major diastereomer as $\Lambda$-Zn-S-L1 for 1 and $\Lambda$-Zn-R-L1 for 2, and the minor diastereomer as $\Lambda$-Zn-S-L1 for 1 and $\Lambda$-Zn-R-L1 for 2 is based on the matching CD spectra and optical rotation with related bis[(R- or S)-N-1-(4-X-phenyl)ethyl-salicylaldiminato-$\kappa^{2}$N,O]zinc(II) complexes ($X = \text{OCH}_3$, Cl, Br) (Scheme 3) [14]. In the latter complexes
the (R) ligand chirality induces a $\Lambda$-Zn configuration and the (S) ligand chirality quantitatively gives the $\Delta$-Zn configuration upon crystallization as deduced from X-ray single crystal studies. At first
sight this may appear similar to compound 1 or 2. For a unifying picture the change in Cahn-Ingold-Prelog (CIP) priority [19] has to
be taken into account, however (see Scheme 4 below). The diaste-
reoselections of the bis[(R- or S)-N-1-(4-X-phenyl)ethyl-salicylaldiminato-$\kappa^{2}$N,O]zinc(II) complexes in CDCl$_3$ solution were
investigated by $^1$H NMR and by vibrational circular dichroism
(VCD) spectroscopy. The appearance of two signals for the Schiff
base imine proton indicated a solution equilibrium of both $\Lambda$- and $\Delta$-Zn diastereomers with a diastereomeric ratio of roughly
80:20% for all three R-configured ligands, correspondingly of
~20:80 for the S-configured ligands. The racemic compound

Fig. 4. $^1$H NMR spectra of R-HL1, and diastereomers $\Delta$/A-Zn-S-L1 (1) and $\Delta$/A-Zn-R-L1 (2) in CDCl$_3$ at 20 °C (spectra were taken within ca. 30 min of solution preparation of 1 or 2).
Δ/Λ- and Λ/Δ-Zn-R/S-L2 (3) also shows the diastereomeric ratio of 67:33% after 40 min in CHCl₃ solution, as evidenced by the presence of two signals for the imine proton in ¹H NMR (Fig. 5). Here we may assign the Δ-S/Δ-R configuration as major diastereomers and the Δ-S/Δ-R configuration as minor diastereomers (Scheme 2), which is based on the solid state X-ray structure where the racemic mixture, that is, enantiomeric pair of the diastereomers Λ-Zn-S-L2 and Δ-Zn-R-L2 are found in the investigated crystal of compound 3 (see below).

To investigate a possible time dependent diastereoselectivity, we ran ¹H NMR spectra of compound 3 in CDCl₃ at different time intervals (Fig. 5). The imine proton shows a single peak at δ 8.27 ppm within ca. 10 min of solution preparation, while after ca. 40 min it shows two broad peaks at δ 8.36 and 8.21 ppm with a ratio of ca. 33:67%. Finally, within ca. 36 h these two peaks are found with a close to unity ratio of ca. 46:54% (Fig. 5).

We assign the single resonance at δ 8.27 ppm shortly after solution preparation in CDCl₃ (ca. 10 min) to the enantiomeric pair Λ-Zn-S-L2 and Δ-Zn-R-L2. The less intense band (33%) at 8.36 ppm is assigned to the newly formed minor Λ-Zn-S-L2 and Δ-Zn-R-L2 diastereomers (cf. Scheme 2). Eventually, after 36 h the ratio between the two enantiomeric pairs Λ-S/Λ-R (54%) versus Δ-S/Δ-R (46%) reaches almost unity. Interestingly however, the ratio does not become exactly 50:50 in the diastereomerization process. Diastereomers Λ-S and Δ-S (also Λ-R and Δ-R) have different relative energies (ΔE) and relative free energies (ΔG) so their Boltzmann weights in equilibrium will not be expected equal [14]. The shift of solution equilibrium to the side of the enantiomeric pair Λ-Zn-S-L2 and Δ-Zn-R-L2 is the basis for its preferential crystallization with concomitant slow enantiomerization in solution as one component is removed from the solution equilibrium.

3.2. Crystal structure of compound 3

Two 2-{(E)-(2-hydroxy-2-phenylethylimino)methyl}phenoxide ligands in compound 3 coordinate to the zinc atom primarily with their imino-nitrogen and phenoxide-oxygen atoms. The two monoanionic N,O-bidentate Schiff base ligands form a distorted N₂O₂-tetrahedral coordination sphere around the zinc atom (Fig. 6). An additional coordination of the two benzyl CH(Ph)OH-oxygen
related ligands based on Ph–C...N=C torsion

\[
\begin{align*}
\text{S-HL1} & : \text{CIP priority: } N > \text{CH}_2\text{OH} > \text{Ph} \\
R-HL2 & : \text{CIP priority: } \text{OH} > \text{CH}_3\text{N} > \text{Ph}
\end{align*}
\]

Table 4

<table>
<thead>
<tr>
<th>Bond Lengths (Å) and Angles (°) in 3</th>
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<tbody>
<tr>
<td>Zn1–O1</td>
</tr>
<tr>
<td>Zn1–O2</td>
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<tr>
<td>Zn1–N1</td>
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<tr>
<td>Zn1–N1</td>
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<tr>
<td>N1–Zn1–O1</td>
</tr>
<tr>
<td>N1–Zn1–O2</td>
</tr>
</tbody>
</table>

\[ 3 \]

\[ \Delta \text{Zn-S-L1} (1) \text{ (by CD and opt. rotation comparison)} \]

\[ \Delta \text{Zn-R-L2} (3) \text{ (by X-ray)} \]

\[ \Delta \text{Zn-R-L} \text{ (by X-ray)} \]

Scheme 4. Correlation of related ligands based on the same Ph–C...N=C torsion with the major Zn–L diastereomer formed. Opposite ligand enantiomers (not shown) give the opposite metal configuration.

For a complete view and explanation the change in CIP priority [19] and the weak Zn–OH coordination (Fig. 6) has been taken into account. The CIP priority changes the absolute configuration from S-HL1 to R-HL2 and R-HL (L = R–N–1-(4-X-phenyl)ethyl-salicylidamine) for ligands with the same Ph–C...C=N torsion (Scheme 4). For these ligands with the same Ph–C...C=N torsion depicted in Scheme 4, the metal-centered chirality is \( \Delta \text{Zn} \) for the L1 and L2 ligands which allow for an additional weak Zn–OH coordination (as found in compound 3) and \( \Lambda \text{Zn} \) for the L ligand without such an additional weak coordination. Hence, the “similarity” in the diastereoselection for \( \Delta \text{Zn-S-L1} \) (1) and \( \Delta \text{Zn-R-L1} \) (2) with \( \Delta \text{Zn-S-L} \) and \( \Delta \text{Zn-R-L} \) from Ref. [14] is superfuous when taking into account the different steric ligand situation for, e. g., S-L1 and S-L with the different Ph–C...C=N torsion. While \( \Delta \text{Zn-S-L1} \) (1) and \( \Delta \text{Zn-R-L1} \) (2) and \( \Delta \text{Zn-R-L2} \) and \( \Delta \text{Zn-S-L2} \) (3), respectively, exhibit indeed the same diastereoselection when taking into account the steric ligand situation with the same Ph–C...C=N torsion for, e. g., S-L1 and R-L2.

Despite the racemic composition, compound 3 crystallizes in the non-centrosymmetric polar space group \( \text{Iba2} \). Accordingly, the molecules must all be oriented in the same direction along the polar axis: The phenyl rings, for example, of the ligands are all pointing in the same direction (along the polar axis) in Fig. 7a. The molecular complexes 3 can be thought of to be arranged in linear chains parallel to the c direction (Zn–Zn = 5.39 Å). This polar packing [33] within the chain in the crystal of 3 probably originates from inter-molecular hydrogen bonding (Fig. 7a). Along such a hydrogen-bonded chain parallel to the c direction the opposite enantiomers alternate (Fig. 7a). The inter-molecular hydrogen bonding \( \text{O2–H}...\text{O1}^\text{ii} \) with \( \text{H}...\text{O1}^\text{ii} = 1.92 \text{ Å, O2–O1}^\text{ii} = 2.72(7) \text{ Å and O2–H...O1}^\text{ii} = 153.5^\circ \) (ii = \( \text{z} + 0.5 \)) is charge-assisted, that is, the hydrogen bond donor and/or acceptor carry positive or negative ionic charges, respectively. Such charge-assisted H-bonds can be much stronger than hydrogen bonds between neutral atoms but can be considered to a distorted octahedral coordination polyhedron with meridional arrangement of the then O,N,O-tridentate ligands. However, the Zn–O2 contacts are substantially longer than the Zn–O1 bonds (Table 4). The complexes sit with their Zn atom on the C2 axis, bisecting the O1–Zn–O1, N–Zn–N and O2–Zn–O2 angles (i = \( \text{z} + 0.5 \)). Irrespective of assuming a pseudo-tetrahedral [4,6,8,14] or octahedral [27–29] ligand arrangement here, the Schiff-base chelate ligands induce axial chirality in the zinc complex 3. Looking along the C2 axis, the two \( \text{N}^\text{O} \)- or \( \text{O}^\text{N} \)-ring planes form propeller blades with either a right- or left-screw orientation. This gives axially chiral \( \Lambda \) or \( \Delta \)-configured metal centers [30] (corresponding to P and M chirality), respectively.

Compound 3 crystallizes in the non-centrosymmetric polar orthorhombic space group \( \text{Iba2} \) (no. 45) which belongs to the crystal class \( \text{mm2} \), where optical activity can occur as specific physical effects [31]. Both optical axes in a single crystal of this optically biaxial orthorhombic system show rotation of the plane of polarization, however, with opposite sign [32]. Because of the dominant effect of double refraction, optical activity can only be measured along the optical axis in many crystal systems [31,32]. Determining the position of the optical axes requires in turn a rather detailed optical study. Therefore, verification of the single-crystal optical activity was not undertaken here.

The \( \text{-CH(Ph)OH} \)-carbon atom in the ligand and the zinc atom are stereogenic centers with \( \text{R} \) and \( \text{S} \) chirality and axial \( \Delta \) and \( \Lambda \) (P and M) chirality, respectively. In the non-enantiomorphous crystal class \( \text{mm2} \) there exists, however, an equal number of oppositely, \( \text{R} \) and \( \text{S} \) and \( \Delta \) and \( \Lambda \) configured centers in the same crystal. This is in agreement with the use of a racemic mixture of the 2-[(E)-(2-hydroxy-2-phenylethylimino)methyl]phenol ligand in the synthesis. For the individual complexes in the solid-state the (S) ligand chirality induces a \( \Lambda \)-Zn configuration and the (R) ligand chirality gives the \( \Delta \)-Zn configuration upon crystallization as deduced from the X-ray single crystal study (Scheme 2). The pseudo-tetrahedral zinc-Schiff base complexes in the crystal lattice must be enantiomeric to each other, in line with the space group symmetry. Note-worthy, the \( \Delta \)-Zn-S-L2 and \( \Delta \)-Zn-R-L2 correlation found here for the major diastereomers in 3 is opposite to those found in \( \Delta \)-bis[(R- or S)-N–1-(4-X-phenyl)ethyl-salicylidinatoκN,O] zinc(II) \((X = \text{OMe, CI, Br}) \) [14] (Scheme 3).
The core of the chains is hydrophilic and wrapped in by hydrophobic phenyl rings (cf. Fig. 7b).

Between adjacent chains no inter-chain π⋯π or no C–H⋯π interactions are found by PLATON despite the presence of phenyl rings [36–38]. Still there is a substantial difference in the inter-chain van-der-Waals or hydrophobic interactions along the a and b axis (Fig. 7 and Scheme 5). Along b adjacent chains can interdigitate and thereby approach more closely (Zn⋯Zn = 9.53 Å). While along a the chains are held at wider distance from each other and can only approach by the tip of the para-phenyl hydrogen atoms (Zn⋯Zn = 13.69 Å). This should correlate with a stronger inter-chain van-der-Waals interactions along b than along a.

Crystal growth is generally favored along the stronger intermolecular interactions. Hydrogen bonding along the c axis leads to a chain packing of the molecular complexes followed by chain interdigititation due to still somewhat stronger van-der-Waals interactions along the b axis. While along a the hydrophobic interactions are even weaker. This then leads to the crystallization of broadened needles to thin plates for compound 3. The packing diagrams of compound 3 in Fig. 7 illustrate the intra-chain and inter-chain packing by hydrophilic and hydrophobic interactions, respectively (cf. Scheme 5). The crystal morphology reflects the supramolecular packing. Face-indexing could not be carried out, due to the poor visibility along the thin dimension of the needle/plate. However, it is safe to assume that the plane of the thin crystals corresponds to the bc-plane with the a-axis orthogonal and along the thin dimensions in 3. Generally, the thin-plate crystal dimension corresponds to the longest crystallographic axis; that is a for compound 3 (cf. Table 1). This longest crystallographic axis can be taken as the packing direction for the chains along a (cf. Scheme 5).

4. Conclusions

Diastereoselection of enantiopure (R or S)-2-[(E)-(2-hydroxy-1-phenylethylimino)methyl]phenol (R- or S-HL1) to pseudotetrahedral Zn(R- or S-HL1)2 leads to Δ-Zn-S-L1 or Δ-Zn-R-L1 as
major and $\Delta$-Zn-S-L1 or $\Delta$-Zn-R-L1 as minor diastereomers. Racemic (R/S)-2-[(2-hydroxy-2-phenylethylimino)methyl]phenol (R/S-HL2) gives the enantiomeric pair $\Lambda$-Zn-S-L2 and $\Lambda$-Zn-R-L2 as major diastereomers and $\Delta$-Zn-S-L2 and $\Delta$-Zn-R-L2 as minor diastereomers. The major racemic enantiomer pair crystallizes in non-centrosymmetric polar space group $iba2$. Time-dependent 1H NMR studies of chloroform solutions of $\Lambda$-Zn-S-L2 / $\Delta$-Zn-R-L2 indicate diastereomerization to $\Delta$-Zn-S-L2 / $\Lambda$-Zn-R-L2 over 36 h with a diastereometric ratio of 54:46.

The CIP priority changes the absolute configuration from $S$-HL1 to R-HL2 by keeping the similar steric ligand situation with the same Ph-C=O=C=N torsion. Therefore, compounds $\Delta$-Zn-S-L1 (1) and $\Delta$-Zn-R-L1 (2) and $\Delta$-Zn-S-L2 and $\Delta$-Zn-R-L2 (3), respectively, exhibit the same major diastereoselection for $S$-L1 and R-L2 or R-L1 and S-L2, respectively. Comparison with other ([(4-X-phenyl)ethenylimino]methyl)phenol ligands (HL) shows a role of the 2-hydroxy group in L1 and L2 for the diastereoselection through weak Zn-OH coordination (as structurally verified in compound $\Lambda$/$\Delta$-Zn-S/R-L2, 3). The racemic compound 3 crystallizes in the non-centrosymmetric polar space group $iba2$ due to identical orientation by intermolecular hydrogen bonding with alternation of the opposite enantiomers along the polar c axis.

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Appendix A. Supplementary material

CCDC 926224 contains the supplementary crystallographic data for 3. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.08.016.

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