Supporting Information for
The selective formation of neutral, heteroleptic zinc(II) complexes via self-discrimination of chiral bisoxazoline racemates and pseudoracemates
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Self-assembly of complexes (S,S)-2 and (S,R)-3. Zn(OAc)₂ (20.2 mg, 0.11 mmol) was added in one portion to a stirred solution (rt) containing (S,S)-1 (33.7 mg, 0.11 mmol, Aldrich Chemicals) and (R,R)-1 (33.7 mg, 0.11 mmol, Aldrich Chemicals) in a degassed mixture of CH₂Cl₂-MeOH (1:1, 6 mL). (Note: For (S,S)-2, the (R,R)-1 was omitted and twice the amount of (S,S)-1 was added.) The resulting clear solution was stirred for 10 minutes and then concentrated under high vacuum. The residue was triturated well with degassed methanol (15 mL) and the resulting solid isolated by filtration and washed with degassed methanol (3 x 10 mL) to afford the zinc complex.

Note. For reference, the NMR spectral data for (R,R)- and (S,S)-1 are: 

(S,S)-2: 59% yield of a colorless solid; mp 185-186 °C (with decomposition); [α]_D²³ = + 684° (c = 0.5, CH₂Cl₂); ¹H NMR (CDCl₃, 600 MHz) 7.15 (br s, 12H), 6.86-6.87 (m, 8H), 4.52 (br dd, J = 8.5, 8.5 Hz, 4H), 4.32 (br dd, J = 8.4, 8.4 Hz, 4H), 3.94 (br s, 2H), 3.76 (br dd, J = 8.3, 8.3 Hz, 4H); ¹³C NMR (CDCl₃, 125 MHz) 171.9, 141.0, 128.5, 127.6, 126.7, 73.3, 65.5, 54.3; FTIR (ATR (ZnSe), wavelength (cm⁻¹), assignment) 2894 (C-H), 1609 (C=N), 1525 (=C-N); LRMS (FAB, m/z) calcd for C₃₉H₃₃N₄O₄Zn (M+H): 675.19, found: 675.2. A sample was recrystallized by slow diffusion of hexane into dichloromethane for x-ray analysis.

X-Ray Structure Determination. A colorless block, with approximate dimensions 0.17 mm x 0.14 mm x 0.05 mm, was mounted on a glass fiber inserted into a tapered copper pin. X-ray intensity data were measured at 100K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a fine-focus Mo-target X-ray tube (λ = 0.71073 Å) operated
at 1500 watts power. A Bruker AXS KRYO-FLEX low temperature device was used to cool the crystal. The crystal-to-detector distance was 4.964 cm.

A hemisphere of data was collected (a total of 1866 frames) using a scan width of 0.3° in ω and an exposure time of 30 sec./frame. Fifty frames were collected to check for decay of the crystal during data collection. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. Integration of the data using an orthorhombic unit cell yielded a total of 60061 reflections to a maximum 2θ angle of 52.74°, of which 13131 were independent (redundancy 4.57%, completeness = 99.9%, Rint = 5.19%, Rsig = 4.30%), and 12539 (95.5%) were greater than 4σ(F). The final cell constants are a = 10.2844(5) Å, b = 16.5841(8) Å, c = 75.389(4) Å, volume = 12858.2(11) Å³. A multi-scan absorption correction was applied using the SADABS program included with SAINT software package.

The structure was solved and refined using the Bruker SHELXL (Version 6.1) software package, using the monoclinic space group C222₁, with Z = 16 for the asymmetric unit C₃₈H₃₄N₄O₄Zn. The final anisotropic full-matrix least-squares refinement on F² converged at R1 = 5.24%, wR2 = 10.37% and a goodness-of-fit of 1.214. The largest peak and hole on the final difference map were 0.544 and −0.632 e/Å³.

(S,R)-3: 68% yield of a colorless solid; mp 271-276 °C (with decomposition); ¹H NMR (CDCl₃, 600 MHz) 7.21-7.29 (m, 12H), 7.04-7.05 (m, 8H), 4.04 (dd, J = 5.2, 8.2 Hz, 2H), 3.87 (dd, J = 8.8, 8.8 Hz, 2H), 3.85 (s, 2H), 3.35 (dd, J = 5.1, 9.0 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) 170.4, 143.8, 128.4, 127.3, 127.0, 72.8, 65.1, 52.7; FTIR (ATR (ZnSe), wavelength (cm⁻¹), assignment) 2899 (C-H), 1699 (s, C=N), 1518 (=C-N); LRMS (FAB, m/z) calcd for C₃₈H₃₅N₄O₄Zn (M+H): 675.19, found: 675.2. A crystal suitable for x-ray analysis was obtained upon standing in the NMR tube (CDCl₃).

X-Ray Structure Determination. A colorless block of approximate dimensions 0.8 mm x 0.5 mm x 0.4 mm was selected and mounted on a glass fiber using 5-minute epoxy. Data were measured at room temperature using a Bruker AXS molybdenum target rotating anode X-ray source (operating at 50kV/40mA) and an 18 cm MarResearch image plate detector. A total of 16914 reflections were collected by oscillation method, resulting in 5045 independent reflections (completeness for theta range 4.26 to 24.40 = 88.6%, redundancy = 3.353, Rint = 3.35 %, Rsig = 2.94 %, of which 4114 (81.5%) were greater than 4σ(F). Monoclinic lattice parameters obtained after refinement using the MarXDS data reduction suite were: a = 17.205(3) Å, b = 10.733(2) Å, c = 18.407(4) Å, β = 105.98(3)°, V = 3267.7(11) Å³. No absorption correction was applied.

The structure was solved and refined with the Bruker AXS SHELXTL software suite using the monoclinic space group P2₁/c, with Z = 4 for the asymmetric unit C₃₈H₃₄N₄O₄Zn. The final anisotropic full-matrix least-squares refinement on F2 converged at R1 = 5.91 %, wR2 =14.08 %, and a goodness-of-fit of 1.124. The largest peak and hole on the final difference map were 0.816 and -0.581.
Self-assembly of complex 6. To a stirred solution (room temperature) of 4(\(S\))-(+)-phenyl-\(\alpha\)-[(4\(S\))-phenyloxazolidin-2-ylidene]-2-oxazolin-2-acetonitrile ((\(S\),\(S\))-4, 36.5 mg, 0.11 mmol, Aldrich Chemicals) and the benzyl-substituted box derivative (\(R\),\(R\))-5 (43.6 mg, 0.11 mmol) in a degassed 1:1 mixture of \(\text{CH}_2\text{Cl}_2\) and MeOH (6 mL) was added Zn(OAc)\(_2\) (20.2 mg, 0.11 mmol) in one portion. The resulting clear solution was stirred for 10 min and then concentrated under vacuum (ca. 0.1 torr). The residue was triturated with degassed methanol (15 mL). The resulting solid separated by filtration, washed with degassed methanol (3 x 10 mL) and dried under vacuum to afford zinc complex 6 (68.8 mg, 79%) as a colorless solid: mp 260-263 °C (dec); [\(\alpha\)]\(_D\) = -203° (c = 0.75, \(\text{CH}_2\text{Cl}_2\)); \(^1\)H NMR (400 MHz, \(\text{CDCl}_3\)) \(\delta\) 7.12-7.29 (m, 17H), 6.91-6.93 (m, 8H), 4.19 (dd, \(J = 5.6, 8.6\) Hz, 2H), 3.96-4.01 (m, 4H), 3.80 (dd, \(J = 8.7, 8.8\) Hz, 2H), 3.54 (d, \(J = 12\) Hz, 1H), 3.60 (d, \(J = 12\) Hz, 1H), 3.24 (dd, \(J = 5.6, 9.5\) Hz, 2H), 3.14 (dd, \(J = 5.4, 9.1\) Hz, 2H); \(^{13}\)C NMR (100 MHz, \(\text{CDCl}_3\)) \(\delta\) 169.9, 168.9, 144.8, 143.6, 141.6, 128.7, 128.6, 127.8, 127.6, 127.1, 126.9, 125.1, 119.6, 73.7, 72.8, 65.8, 65.7, 65.4, 47.5, 31.4; HRMS (FAB, \(m/z\)) calcd for C\(_{46}\)H\(_{40}\)N\(_5\)O\(_4\)Zn (M+H) 790.2372, found 790.2367 \(m/z\). A sample was recrystallized from hot methanol for x-ray analysis.

X-Ray Structure Determination. A colorless block, with approximate dimensions 0.33 mm x 0.23 mm x 0.13 mm, was mounted on a glass fiber inserted into a tapered copper pin. X-ray intensity data were measured at 100K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a fine-focus Mo-target X-ray tube (\(\lambda = 0.71073\) Å) operated at 1500 watts power. A Bruker AXS KRYO-FLEX low temperature device was used to cool the crystal. The crystal-to-detector distance was 5.944 cm.

A sphere of data was collected (a total of 2474 frames) using a scan width of 0.3° in \(\omega\) and an exposure time of 20 sec/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. Integration of the data using an orthorhombic unit cell yielded a total of 23488 reflections to a maximum \(2\theta\) angle of 56.58°, of which 17235 were independent (redundancy 1.363, completeness = 94.3%, \(R_{int} = 1.64\)%, \(R_{sig} = 3.94\)%), and 16737 (97.1%) were greater than 4\(\sigma\)(F). The final cell constants are \(a = 10.8664(6)\) Å, \(b = 10.8866(6)\) Å, \(c = 17.2241(9)\) Å, \(\alpha = 73.1460(10)\)°, \(\beta = 88.6230(10)\)°, \(\gamma = 86.9430(10)\)°, volume = 1933.32(18) Å\(^3\). A multi-scan absorption correction was applied using the SADABS program included with SAINT software package.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) software package, using the monoclinic space group P1, with \(Z = 1\) for the asymmetric unit C\(_{22}\)H\(_{18}\)N\(_{10}\)O\(_8\)Zn\(_2\) (the asymmetric unit is represented by two molecules). The final anisotropic full-matrix least-squares refinement on \(F^2\) converged at \(R_1 = 3.78\)%, \(wR_2 = 9.03\)% and a goodness-of-fit of 1.046. The largest peak and hole on the final difference map were 0.605 and –0.348 e/Å\(^3\).
**Preparation of (R,R)-5.** To a cooled (-78 °C), stirred solution of n-BuLi (2.61 mL of a 2.5 M solution in hexanes, 6.52 mmol), diisopropylamine (0.456 mL, 3.26 mmol), and TMEDA (0.892 mL, 6.52 mmol) in a mixture of dry THF (10 mL) and DMPU (15 mL) was added dropwise a solution of 2,2'-methylenebis((4R)-4-phenyl-4,5-dihydro-2-oxazole (2.2 g, 7.18 mmol) in a mixture of dry THF (10 mL) and DMPU (5 mL). The mixture was stirred for 2 h (-78 °C) during which time a pale-yellow solution formed. Afterwards, a solution of benzyl bromide (1.12 g, 6.55 mmol) in a mixture of dry THF (15 mL) and DMPU (5 mL) was added dropwise. The resulting mixture was allowed to slowly warm to room temperature with stirring for 12 h. The resulting mixture was quenched by the addition of aqueous ammonium chloride solution (ca 50 mL) and extracted with CH₂Cl₂ (2 x 120 mL). The combined organic phases were washed with brine, dried with anhydrous sodium sulfate, and concentrated under vacuum. The residual DMPU was removed under high vacuum (110 °C @ 1 torr) and the crude product purified by flash column chromatography on silica (eluent: 95:5 CH₂Cl₂:MeOH) to afford (R,R)-5 as a light yellow liquid (2.22 g, 78 %). ¹H NMR (400 MHz, CDCl₃) δ 7.15-7.28 (m, 13H), 6.89-6.91 (m, 2H), 5.13-5.17 (m, 2H), 4.59 and 4.62 (overlapping dd, J = 10.1, 10.1 Hz, 2H), 4.10 and 4.12 (overlapping dd, J = 8.1, 8.2 Hz, 1H), 3.99 and 4.02 (overlapping dd, J = 8.3, 8.3 Hz, 2H), 3.33-3.42 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 165.3, 141.9, 141.8, 137.8, 129.1, 128.6, 128.5, 127.5, 127.4, 126.7, 126.6, 126.5, 75.3, 75.1, 69.5, 69.4, 41.3, 35.6; HRMS (FAB, m/z) calcd for C₂₆H₂₄N₂O₂ (M+H): 397.1916, found: 397.1903 m/z.

Copies of spectra follow.

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