

# Synthesis, Characterization, and Structure of Macrocyclic Mono- and $C_2$ -Symmetric, Binuclear Nickel Calixsalen Complexes

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Mono- (**3a,b**) and binuclear (**4a,b**) tetradentate Ni<sup>II</sup> complexes of a series of 26-membered macrocyclic salen dimers, [salen(CH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>, are prepared in good yield by solvent-controlled reaction with Ni(OAc)<sub>2</sub>. The mononuclear complex **3b** crystallizes in the trigonal space group  $3P_1(\#144)$ ,  $a = 18.2566(2)$  Å,  $c = 15.9244(2)$  Å,  $V = 4596.57(8)$  Å<sup>3</sup>, and  $Z = 3$ . Refinement converged with  $R = 0.054$  and  $R_w = 0.049$  for 6852 reflections with  $I > 2.003\sigma(I)$ . The Ni<sup>II</sup> in complex **3b** coordinates in an approximate square planar geometry to one of the two available tetradentate salen sites. Complex **4b** crystallizes in the orthorhombic space group  $P2_12_12_1(\#19)$ ,  $a = 19.531(2)$  Å,  $b = 22.891(3)$ ,  $c = 13.373(1)$  Å,  $V = 5960(1)$  Å<sup>3</sup>, and  $Z = 4$ . The refinement converged with  $R = 0.067$  and  $R_w = 0.065$  for 3752 reflections with  $I > 2.003\sigma(I)$ . Complex **4b** coordinates two distorted square planar, cofacially oriented Ni<sup>II</sup>–salen units held 7.1 Å apart by a rigid, syn-folded macrocyclic structure. The solution spectroscopic data and solid-state crystallographic data of **3b** and **4b** demonstrate the presence of a molecular-sized cavity which shows host–guest properties. Reaction of the flexible 32-membered disalen macrocycle [salen(OCH<sub>2</sub>CH<sub>2</sub>O)]<sub>2</sub> with Ni(OAc)<sub>2</sub> resulted in formation of a binuclear complex, **5**. Complex **5** crystallizes in the triclinic space group  $P1(\#1)$ ,  $a = 10.366(4)$  Å,  $b = 12.170(3)$  Å,  $c = 10.021(2)$  Å,  $\alpha = 106.29(2)^\circ$ ,  $\beta = 91.69(2)^\circ$ ,  $\gamma = 68.63(2)^\circ$ ,  $V = 1126.3(5)$  Å<sup>3</sup>, and  $Z = 1$ . The refinement converged with  $R = 0.052$  and  $R_w = 0.053$  for 2385 reflections with  $I > 2.003\sigma(I)$ . The binuclear complex **5** contains two cofacially oriented, square planar Ni<sup>II</sup>–salen groups lying 3.5 Å apart in an anti-folded macrocyclic structure.

## Introduction

Synthetic molecular receptors based on macrocyclic mono- and binuclear coordination complexes with a well-defined chiral cavity are of interest in the context of supramolecular chemistry.<sup>1–3</sup> Examples housing one or more catalytically active transition metal sites embedded in a rigid, chiral matrix have been used as artificial enzymes,<sup>4–8</sup> which model the putative active site for a number of important biological systems.<sup>9,10</sup> These examples are particularly informative because with their use, examination of complementary host–guest chemistry<sup>11</sup> accruing from a range of noncovalent interactions becomes feasible.

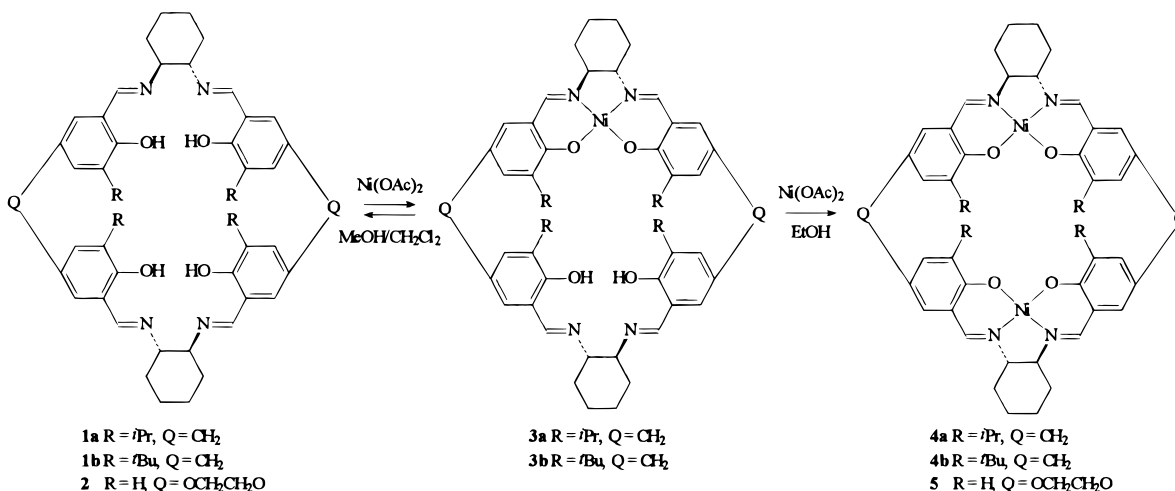
There is a long-standing interest in macrocyclic Schiff base complexes<sup>5,12–35</sup> in this regard because reliable synthetic avenues

leading to a variety of diverse structural types have been developed. Our approach to the discovery of new, functional, chiral transition-metal complexes focuses on synthesis of metal-

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Scheme 1. Preparation of the Mono- and Binuclear Ni<sup>II</sup> Calixsalen Complexes

free, chiral, macrocyclic ligands containing two tetradentate, salen coordination sites embedded in a molecular-sized cavity. Subsequent, controlled complexation with transition metal ions may allow preparation of monometallic as well as homo- and heterobimetallic, macrocyclic, chiral salen complexes with potential applications in catalysis<sup>36–39</sup> and as biomimetics.<sup>4,40,41</sup>

Previously, we reported<sup>42</sup> the synthesis of novel macrocyclic, chiral “calixsalens”, prepared by templated Schiff base condensation<sup>12,43</sup> of (*R,R*)- or (*S,S*)-cyclohexane-1,2-diamine and an appropriate dialdehyde in the presence of Ba<sup>II</sup>. Although we were unable to fully structurally characterize their corresponding dimanganese complexes, we described their activity as catalysts for enantioselective styrene epoxidation. Herein, we describe the preparation as well as the spectroscopic and crystallographic characterization of a number of calixsalen mono- and binuclear Ni<sup>II</sup> complexes (Scheme 1) which are good structural models for the dimanganese calixsalen enantioselective epoxidation catalysts.

## Experimental Section

**General.** The tartrate salt of (*R,R*)-1,2-cyclohexanediamine was received as a gift from Sepracor Canada. The enantiopure free amine was isolated by the standard procedure.<sup>44</sup> All other chemicals and solvents were purchased from Aldrich and used as received. Reactions were performed at room temperature without protection from air. Flash column chromatographic separations used MERCK silica gel (230–400 mesh). Elementary analyses were performed by the Analytical Service Laboratory in the Department of Chemistry, University of

Alberta. Electrospray mass spectra (ESMS) were measured at the Biochemical Mass Spectroscopy Laboratory at the Department of Chemistry, University of Waterloo. Infrared spectra were recorded on a Mattson Polaris Fourier transform spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured in CDCl<sub>3</sub>, CD<sub>3</sub>COCD<sub>3</sub>, or CD<sub>2</sub>Cl<sub>2</sub> on a GE 300-NB instrument operating at 300.1 MHz. Chemical shifts for <sup>13</sup>C NMR spectra are relative to the solvent: δ = 77.2 ppm for CDCl<sub>3</sub> or δ = 54.0 ppm for CD<sub>2</sub>Cl<sub>2</sub>. Proton chemical shift data were referenced to internal Me<sub>4</sub>Si and are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, br = broad, m = multiplet), coupling constant (*J*, Hz), and integration. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were processed using NUTS software (Acorn NMR). The ligands **1a**, **1b**, and **2** were prepared as described previously.<sup>42</sup>

**Mononuclear Nickel Complexes.** To a yellow solution of ligand **1a** or **1b** (0.056 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added a solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (2 equiv., 0.028 g, 0.11 mmol) dissolved in a minimal amount of MeOH. The resulting red reaction mixture was stirred for 4 h at room temperature. Additional CH<sub>2</sub>Cl<sub>2</sub> was added as necessary to dissolve any precipitate that formed. Removing volatiles with an oil pump vacuum and extracting the resulting crude product with 2 × 4 mL portions of CH<sub>2</sub>Cl<sub>2</sub> gave a red solution which was purified by flash chromatography on a silica gel column. Initial elution with CH<sub>2</sub>Cl<sub>2</sub> separated unreacted free ligand. Continued elution with MeOH moved an orange band which left the product as an orange-yellow solid on removal of solvent.

**(*R,R*)-3a.** Yield: 0.038 g, 76%. IR (Nujol): 1628 (CH=N), 1603 (CH=N), 1538 (Ph), 1319, 1288, 1263, 1233, 1170, 1152, 1109, 1049, 1019, 946, 908, 764, 772, 736, 724 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 13.09 (s, 1H, OH), 13.04 (s, 1H, OH), 8.45 (s, 1H), 8.29 (s, 1H), 7.43 (d, *J* = 2.1, 1H), 7.21 (d, *J* = 2.1, 1H), 7.19 (d, *J* = 1.8, 1H), 7.09 (d, *J* = 2.4, 1H), 7.02 (d, *J* = 2.4, 1H), 6.88 (d, *J* = 1.8, 1H), 6.82 (d, *J* = 2.1, 1H), 6.69 (d, *J* = 2.1, 1H), 6.28 (d, *J* = 2.1, 1H), 6.08 (d, *J* = 1.8, 1H), 5.31 (s, 1H), 3.84 (m, 4H), 3.65 (br, 1H), 3.43 (m, 4H, CHMe<sub>2</sub>), 3.25 (s, 1H), 3.21 (s, 1H), 2.64 (br, 1H), 2.31–2.24 (br, 2H), 1.97–1.92 (br, 6H), 1.72 (br, 4H), 1.35–1.28 [m, 12H, (CHMe<sub>2</sub>)], 1.17–1.08 [m, 12H, (CHMe<sub>2</sub>)]. <sup>13</sup>C{<sup>1</sup>H}NMR (CDCl<sub>3</sub>): δ 166.6, 166.4, 164.2, 163.1, 161.8, 156.2, 141.4, 140.7, 135.7, 134.1, 133.2, 132.2, 130.1, 129.6, 129.3, 129.0, 125.9, 125.8, 121.7, 118.2, 72.4, 72.0, 71.9, 67.7, 39.6, 39.2, 30.0, 28.0, 27.6, 27.3 (CHMe<sub>2</sub>), 26.7 [(CHMe<sub>2</sub>)], 26.6 [(CHMe<sub>2</sub>)], 25.1, 24.5, 23.0 [(CHMe<sub>2</sub>)], 22.8 [(CHMe<sub>2</sub>)], 22.7 [(CHMe<sub>2</sub>)], 22.5 [(CHMe<sub>2</sub>)], 21.4. Anal. Calcd for C<sub>54</sub>H<sub>70</sub>O<sub>4</sub>N<sub>4</sub>Ni·2H<sub>2</sub>O: C, 69.75; H, 7.37; N, 6.03. Found: C, 70.06; H, 7.27; N, 5.91.

**(*R,R*)-3b.** Yield: 0.043 g, 82%. IR (Nujol): 1628 (CH=N), 1536 (Ph), 1318, 1271, 1271, 1239, 1206, 1172, 1021, 946, 908, 789, 736 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 13.32 (s, 1H OH), 13.21 (s, 1H, OH), 8.42 (s, 1H), 8.20 (s, 1H), 7.39 (s, 1H), 7.24 (d, *J* = 2.1, 1H), 7.22 (d, *J* = 1.5, 1H), 7.07 (br, 2H), 6.88 (s, 2H), 6.68 (d, *J* = 2.7, 1H), 6.23 (s, 1H), 5.98 (s, 1H), 3.81 (s, 4H), 3.61 (br, 1H), 3.26 (s, 1H), 3.16 (s, 1H), 2.68 (br, 1H), 2.30–2.23 (br, 2H), 2.18–1.85 (br, 4H), 1.73–

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**Table 1.** Crystallographic Data for **3b**, **4b**, and **5**

	<b>3b</b>	<b>4b</b>	<b>5</b>
empirical formula	C <sub>58</sub> H <sub>74.50</sub> O <sub>4.25</sub> N <sub>4</sub> Ni <sub>2</sub>	C <sub>60.70</sub> H <sub>83.40</sub> O <sub>4</sub> N <sub>5</sub> Ni <sub>2</sub> Cl <sub>1.40</sub>	C <sub>46</sub> H <sub>48</sub> N <sub>4</sub> O <sub>8</sub> Ni <sub>2</sub> Cl <sub>4</sub>
fw	954.45	1114.19	1044.12
space group	<i>P</i> 3 <sub>1</sub> (No. 144)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)	<i>P</i> 1 (No. 1)
<i>T</i> (°C)	−60 ± 1	26 ± 1	26 ± 1
$\lambda$ (Å)	0.71069	1.54178	0.71069
<i>a</i> (Å)	18.2566(2)	19.531(2)	10.366(4)
<i>b</i> (Å)		22.819(3)	12.170(3)
<i>c</i> (Å)	15.9244(2)	13.373(1)	10.021(2)
$\alpha$ (deg)			106.29(2)
$\beta$ (deg)			91.69(2)
$\gamma$ (deg)			68.63(2)
<i>V</i> (Å <sup>3</sup> )	4596.57(8)	5960(1)	1126.3(5)
<i>Z</i>	3	4	1
$\rho_{\text{calcd}}$ (g/cm <sup>3</sup> )	1.034	1.242	1.539
$\mu$ (cm <sup>−1</sup> )	3.59	17.35	11.32
<i>R</i> <sup>a</sup>	0.054	0.067	0.052
<i>R</i> <sub>w</sub> <sup>b</sup>	0.049	0.065	0.053

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum w|F_o|^2]^{1/2}.$$

1.62 (br, 2H), 1.48 [s, 9H, (CMe<sub>3</sub>)], 1.47 [s, 9H, (CMe<sub>3</sub>)], 1.37 s, 9H, (CMe<sub>3</sub>), 1.27 [s, 9H, (CMe<sub>3</sub>)]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$  167.8, 167.3, 166.0, 165.0, 164.0, 158.7, 158.5, 157.8, 142.2, 141.4, 137.2, 137.0, 135.0, 134.4, 134.3, 133.0, 131.8, 131.0, 130.9, 130.5, 130.4, 126.0, 125.6, 123.5, 122.9, 119.9, 119.5, 73.2, 72.5, 71.2, 68.7, 40.2, 39.6, 35.9 [(CMe<sub>3</sub>)], 35.8 [(CMe<sub>3</sub>)], 35.4 [(CMe<sub>3</sub>)], 31.0 [(CMe<sub>3</sub>)], 28.5 [(CMe<sub>3</sub>)], 28.4 [(CMe<sub>3</sub>)], 25.8, 25.2, 22.0; remaining carbon signals were obscured by solvent. Anal. Calcd for C<sub>58</sub>H<sub>74</sub>O<sub>4</sub>N<sub>4</sub>Ni<sub>2</sub>·H<sub>2</sub>O: C, 71.97; H, 7.91; N, 5.99. Found: C, 71.74; H, 7.97; N, 5.58.

**Bimetallic Nickel Complexes.** To a solution of ligand **1a**, **1b**, or **2** (0.030 mmol) in a minimal amount of CHCl<sub>3</sub> was added a solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.030 g, 4 equiv, 0.12 mmol) in hot EtOH (2 mL). After addition, the CHCl<sub>3</sub> was removed under a vacuum and the remaining solution was stirred for an additional 2 h. The resultant red precipitate was collected by filtration and washed with EtOH (3 × 5 mL). Crystallization from CH<sub>3</sub>CN/EtOH/CH<sub>2</sub>Cl<sub>2</sub> (0.5:1:1) afforded dark red crystals suitable for X-ray diffraction. The deep-red crystals of **5** are very sparingly soluble in common organic solvents.

**(R,R)-4a.** Yield: 0.026 g, 92%. IR (Nujol): 1629 (CH=N), 1613 (CH=CN), 1542 (Ph), 1344, 1285, 1232, 1160, 1107, 1060, 954, 902, 875, 783, 730, 697 cm<sup>−1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.28 (s, 2H), 6.95 (d, *J* = 1.8, 2H), 6.84 (d, *J* = 2.4, 2H), 6.82 (d, *J* = 2.4, 2H), 6.67 (d, *J* = 2.1, 2H), 6.60 (d, *J* = 2.1, 2H), 3.60 (m, 2H), 3.57 (d, *J* = 12.6, 2H), 3.46 (d, *J* = 12.3, 2H), 3.20 (m, 4H, CHMe<sub>2</sub>), 2.42 (br, 2H), 2.23–2.10 (br, 4H), 1.86 (br, 4H), 1.43–1.36 (m, 8H), 1.02–0.89 (m, 24H, CHMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  164.5, 164.4, 163.7, 156.7, 141.4, 141.2, 131.3, 131.1, 130.6, 130.0, 128.0, 126.1, 124.3, 122.7, 72.0, 67.6, 42.3, 30.6, 28.0, 26.6 (CHMe<sub>2</sub>), 26.2 (CHMe<sub>2</sub>), 25.6, 24.8, 23.5 (CHMe<sub>2</sub>), 23.3 (CHMe<sub>2</sub>), 23.1 (CHMe<sub>2</sub>), 22.9 (CHMe<sub>2</sub>). Anal. Calcd for C<sub>54</sub>H<sub>68</sub>O<sub>4</sub>N<sub>4</sub>Ni<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 63.79; H, 6.42; N, 5.41. Found: C, 63.10; H, 6.53; N, 5.36.

**(R,R)-4b.** Yield: 0.028 g, 94%. IR (Nujol): 1632 (CH=N), 1612 (CH=CN), 1535 (Ph), 1318, 1271, 1239, 1206, 1166, 1100, 1060, 1027, 942, 868, 776, 724, 690 cm<sup>−1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.25 (d, *J* = 1.8, 2H), 6.96 (d, *J* = 2.4, 2H), 6.84 (d, *J* = 1.2, 2H), 6.83 (d, *J* = 2.4, 2H), 6.63 (d, *J* = 2.4, 2H), 6.55 (d, *J* = 2.4, 2H), 3.55 (m, 2H), 3.54 (d, *J* = 12.3, 2H), 3.44 (d, *J* = 12.3, 2H), 2.54 (br, 2H), 2.20–2.11 (br, 4H), 1.87–1.44 (br, 4H), 1.41–1.10 (m, 8H), 1.23 (s, 18H, CMe<sub>3</sub>), 1.05 (s, CMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  165.7, 165.6, 163.5, 156.5, 142.1, 141.6, 131.7, 131.5, 130.1, 128.2, 126.3, 123.5, 123.3, 71.6, 67.9, 42.1, 35.5 (CMe<sub>3</sub>), 35.4 (CMe<sub>3</sub>), 31.1 (CMe<sub>3</sub>), 30.9, 30.5 (CMe<sub>3</sub>), 28.2, 25.6, 24.9. Anal. Calcd for C<sub>58</sub>H<sub>72</sub>O<sub>4</sub>N<sub>4</sub>Ni<sub>2</sub>·H<sub>2</sub>O: C, 67.9; H, 7.28; N, 5.47. Found: C, 67.51; H, 6.50; N, 5.19.

**5 ESMS.** Calcd for C<sub>44</sub>H<sub>44</sub>N<sub>4</sub>O<sub>8</sub>Ni<sub>2</sub>: *m/z* = 872. Found: 872.78, 874.81, 875.71, 876.72. IR (neat): 1649 (CH=N), 1568 (Ph), 1556, 1483, 1431, 1285, 1225, 1172, 1407, 882, 822, 697, 618, 565, 472 cm<sup>−1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  6.74 (m, 6H), 6.52 (m, 6H), 5.90 (d, *J* = 3.3, 2H), 5.79 (d, *J* = 2.7, 2H), 4.38 (m, 8H), 3.28 (m, 4H); remaining cyclohexyl resonances were obscured by impurities.

**<sup>1</sup>H NMR Titration Experiments.** Aliquots of a solution of the guest (2.5 mol/L) in CDCl<sub>3</sub> were added, using a 25  $\mu$ L syringe, to a 0.5-mL CDCl<sub>3</sub> host solution (0.025 mmol/L) at room temperature. The <sup>1</sup>H NMR spectra of the resultant mixture were then recorded every 10 min after each addition. The association constant, *K*<sub>a</sub>, was determined by integration of the free imine signals of both free host and its host–guest complex. Measurements were made in triplicate with an estimated error of  $\pm 10\%$ .

**X-ray Crystallography.** The crystal data for complexes **3b**, **4b**, and **5** are given in Table 1. Data for crystal **3b** were collected on a Siemens P4 diffractometer equipped with a SMART CCD detector (Mo K $\alpha$ ,  $\lambda$  = 0.71069 radiation) and a rotating anode generator at a temperature of  $-60 \pm 1$  °C. The hemisphere of data was collected with 30-s, 0.3-deg frames to a 2 $\theta_{\text{max}}$  = 55.15°. Data for **4b** and **5** were collected on a Rigaku AFC6S diffractometer (Cu K $\alpha$ ,  $\lambda$  = 1.54178 Å or Mo K $\alpha$ ,  $\lambda$  = 0.71069 Å radiation). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 (**4b**) or 16 (**5**) carefully centered reflections in the range of 54.80 < 2 $\theta$  < 59.68° (**4b**) or 20.47 < 2 $\theta$  < 22.84° (**5**). The data were corrected for Lorentz and Polarization effects, and a correction for secondary extinction was applied for **4b**. The intensities of these representative reflections were measured after every 150 reflections. No decay was evident over the course of data collection for **4b**. Because of slow decay, a linear correction factor was applied to the data of **5**.

The structures **3b**, **4b**, and **5** were all solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically, except for **5**. Hydrogens were optimized by positional refinement, with isotropic thermal parameters set 20% greater than those of their bonding partners at the time of their inclusion. However, parameters were fixed for the final round of refinement. The final cycle of full-matrix, least-squares refinement for **3b** yielded final *R* = 0.054 and *R*<sub>w</sub> = 0.049 based on 4162 unique observations (*I* > 1.50  $\sigma(I)$ ). The final *R* and *R*<sub>w</sub> factors of **4b** and **5** (Table 1) were obtained from the final cycle of full-matrix, least-squares refinement based on 3752 (**4b**) or 2385 (**5**) observed reflections (*I* > 2.00  $\sigma(I)$ ). The maximum and minimum residual electron densities for **3b**, **4b**, and **5** were 0.53/−0.31 e<sup>−</sup>/Å<sup>3</sup>, 0.89/−0.61 e<sup>−</sup>/Å<sup>3</sup>, and 0.55/−0.43 e<sup>−</sup>/Å<sup>3</sup>, respectively. Crystal data and details of the structure determinations are given in Table 1.

Neutral atom scattering factors were taken from Cromer and Waber.<sup>45</sup> All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1997). Atomic coordinates and selected bond distances for **3b**, **4b**, and **5** are given in Tables 2 and 3.

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**Table 2.** Selected Bond Distances (Å)

				<b>3b</b>			
Ni(1)–O(1)	1.867(4)	Ni(1)–O(4)	1.854(5)	Ni(1)–N(3)	1.862(5)	Ni(1)–N(4)	1.838(6)
N(1)–C(14)	1.276(8)	N(2)–C(21)	1.281(7)	N(3)–C(35)	1.288(7)	N(4)–C(42)	1.313(8)
				<b>4b</b>			
Ni(1)–O(1)	1.853(4)	Ni(1)–O(2)	1.869(5)	Ni(1)–N(1)	1.853(6)	Ni(1)–N(2)	1.874(5)
Ni(2)–O(3)	1.855(4)	Ni(2)–O(4)	1.852(5)	Ni(2)–N(3)	1.829(5)	Ni(2)–N(4)	1.837(5)
				<b>5</b>			
Ni(1)–O(1)	1.86(1)	Ni(1)–O(8)	1.84(1)	Ni(1)–N(3)	1.81(1)	Ni(1)–N(4)	1.84(1)
Ni(2)–O(4)	1.85(1)	Ni(2)–O(5)	1.84(1)	Ni(2)–N(1)	1.89(1)	Ni(2)–N(2)	1.87(1)
N(1)–C(15)	1.24(2)	N(2)–C(22)	1.28(2)	N(3)–C(37)	1.32(2)	N(4)–C(44)	1.30(2)

**Table 3.** Selected Bond Angles in Complexes **3b**, **4b**, and **5**

						<b>3b</b>	
O(1)–Ni(1)–O(4)	89.0(2)	O(1)–Ni(1)–N(3)	174.0(2)	O(1)–Ni(1)–N(4)	91.3(2)		
O(4)–Ni(1)–N(3)	94.3(2)	O(4)–Ni(1)–N(4)	179.1(3)	N(3)–Ni(1)–N(4)	85.4(2)		
C(14)–N(1)–C(15)	116.5(5)	C(20)–N(2)–C(21)	118.1(5)				
						<b>4b</b>	
O(1)–Ni(1)–O(2)	88.8(2)	O(1)–Ni(1)–N(1)	93.4(2)	O(1)–Ni(1)–N(2)	166.6(2)		
O(2)–Ni(1)–N(1)	174.1(2)	O(2)–Ni(1)–N(2)	93.1(2)	N(1)–Ni(1)–N(2)	86.0(2)		
O(3)–Ni(2)–O(4)	90.3(2)	O(3)–Ni(2)–N(3)	92.0(2)	O(3)–Ni(2)–N(4)	168.2(2)		
O(4)–Ni(2)–N(3)	172.7(2)	O(4)–Ni(2)–N(4)	93.4(2)				
						<b>5</b>	
O(1)–Ni(1)–O(8)	84.8(5)	O(1)–Ni(1)–N(3)	176.0(6)	O(1)–Ni(1)–N(4)	95.3(6)		
O(8)–Ni(1)–N(3)	93.1(6)	O(8)–Ni(1)–N(4)	178.8(5)	N(3)–Ni(1)–N(4)	86.9(6)		
O(4)–Ni(2)–O(5)	84.5(5)	O(4)–Ni(2)–N(1)	96.4(6)	O(4)–Ni(2)–N(2)	176.1(5)		
O(5)–Ni(2)–N(2)	93.4(6)	N(1)–Ni(2)–N(2)	85.9(6)				

## Results and Discussion

**Preparation.** The yellow calixsalens **1a** and **1b** readily coordinate Ni<sup>II</sup> to form bright-red products; however, the outcome of complexation was found to be strongly solvent-dependent (Scheme 1). The major products formed from reaction of the macrocyclic disalens **1a** and **1b** in methanol/methylene chloride solvent mixtures were identified as the mononuclear Ni<sup>II</sup> complexes **3a** and **3b**, respectively, which were isolated by chromatography in 80–85% yield. The corresponding mononuclear complex could not be isolated from the reaction of the ethylene glycol linked disalen **2** (Scheme 1). Complexation of **1a,b** at higher temperature (50 °C) also gave mononuclear Ni(II) complexes in methanol/methylene chloride. Increasing the reaction time from 4 to 24 h at 50 °C in the presence of excess Ni(OAc)<sub>2</sub> led to ring-opened complexes which showed <sup>1</sup>H NMR signals assigned to free OH (11.67 ppm) and CHO (9.80 ppm). A significant amount of free ligand remained during the reaction, as observed by TLC, suggesting that coordination is reversible in solution. This assumption was also supported by the observation that the characteristic imine signal of the free ligand was observed in the <sup>1</sup>H NMR spectrum after storing a pure sample of the mononuclear **3b** in CDCl<sub>3</sub> over a period of 1 week. In contrast, the complexes appeared to be completely stable in air at room temperature in the solid state.

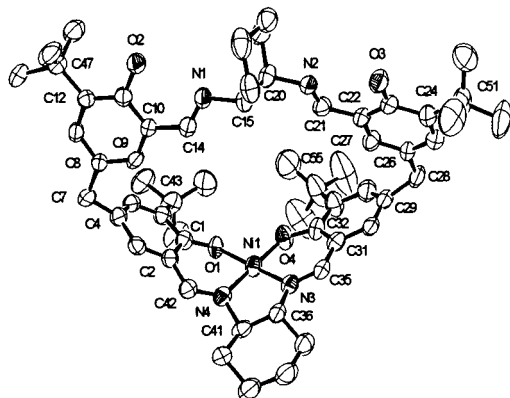
Complexation of calixsalens **1a**, **1b**, or **2** with Ni(OAc)<sub>2</sub> in ethanol at room temperature afforded the corresponding binuclear Ni<sup>II</sup> complexes **4a**, **4b**, or **5** as red precipitates in good yield (Scheme 1). The binuclear complexes are much less soluble than their related mononuclear complexes, and hence the coordination equilibrium shifts in favor of **4a** and **4b**, which are isolated to the exclusion of **3a** and **3b**. The dinuclear complexes **4a** and **4b** were also obtained by stepwise Ni<sup>II</sup> coordination. Thus, treatment of the mononuclear complexes **3a** or **3b** with a second equivalent of Ni(OAc)<sub>2</sub> gave **4a** and **4b** in good yield (Scheme 1).

**Solution Structure of the Mononuclear Calixsalen Complexes.** Coordination of the calixsalens **1a** and **1b** is surprisingly

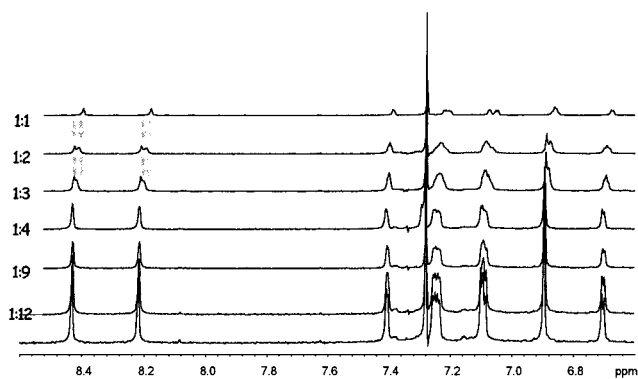
facile considering that the 1,3-dialternate conformation of the free ligand<sup>42</sup> requires considerable molecular reorganization to present a tetradentate O,N,N,O-ligand set to the metal. Solution NMR spectra of **3a** and **3b** were consistent with coordination of a single Ni<sup>II</sup> to give a planar, diamagnetic structure. Proton and carbon NMR chemical shift assignments were confirmed by 2D <sup>1</sup>H–<sup>13</sup>C correlation experiments. Typically, two low field <sup>1</sup>H NMR signals assigned to two free OH groups in the uncoordinated salen site were observed at ca. 13 ppm. Resonances assigned to the two corresponding nonequivalent free imine protons were observed at ca. 8 ppm, whereas the complexes' CH=N protons were shifted considerably upfield (7.09 ppm, 7.43 ppm in **3a** and 7.07 ppm, 7.39 ppm in **3b**). Consistent with C<sub>1</sub> symmetry, eight <sup>1</sup>H aromatic resonances and a total of 50 <sup>13</sup>C resonances were observed in the NMR spectra of **3a** and **3b**. Complete assignments are given in the Experimental Section.

**Solid-State Structure of 3b.** A dark-red crystal was grown by slow evaporation of a solution of **3b** in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (1:1) at room temperature over a 1-month period. The molecular structure of **3b** (Figure 1) shows that a single Ni<sup>II</sup> atom coordinates to one of the two available salen sites. Consistent with their diamagnetism, the four salen donor atoms coordinate to give a square planar complex, as is evident by consideration of the bond angles O(1)–Ni–N(3), 174.0°; O(4)–Ni–N(4), 179.1°; O(1)–Ni–O(4), 89.0°; and N(3)–Ni–N(4), 85.4°(Table 1). The average bond distances for O–Ni, 1.86 Å, and N–Ni, 1.85 Å (Table 2) compare favorably with values of reported monomeric salen Ni<sup>II</sup> complexes.<sup>46</sup> Steric demands of the two *tert*-butyl groups force the two phenol groups in the uncoordinated salen site to remain anti to one another, as is the case in the free calixsalen ligand.<sup>42</sup> Unlike the free calixsalen,<sup>42</sup> the *trans*-1,3-diaminocyclohexane groups in the uncoordinated salen site of **3b** are forced to assume an unfavorable diaxial conformation to relieve angle strain in the ring caused by the forced planarity of the coordinated salen site.

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**Figure 1.** ORTEP representation of the mononuclear nickel complex **3b**.



**Figure 2.** Expanded  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  vs mole ratio of **3b**/acetone.

Examination of the solid-state conformation of **3b** (Figure 1) shows that an approximate plane containing the uncoordinated salen site is orthogonal to the plane containing the coordinated salen site. As a consequence, the imine hydrogens and one aromatic hydrogen on each of the two phenyl groups connected to the uncoordinated salen site are oriented directly toward the center of the cavity. Approximate calculations based on the structure in Figure 1 suggest a cavity size of approximately  $6.3 \times 4.5 \text{ \AA}$ .

**Host–Guest Chemistry of 3d.** Addition of acetone to a  $\text{CDCl}_3$  solution of **3b** resulted in substantial changes of the proton chemical shifts as well as the splitting pattern, especially for the imine and the aromatic protons.  $^1\text{H}$  NMR titration experiments with acetone indicated that the chemical shifts of the free imine as well as the aromatic protons of the complex **3b** shifted upfield by about 0.05–0.07 ppm while the chemical shifts of the complexed imines remained unchanged (Figure 2). We interpret the observed changes in the proton chemical shifts in terms of a 1:1 host–guest complex formation between the host **3b** and the guest acetone. Integration of the proton NMR spectrum gave a value for the association constant,  $K_a$ , of  $1.5 \times 10^5 \text{ Lmol}^{-1}$ . Because only the chemical shifts of those protons close to the cavity changed, it is unlikely that the acetone guest molecule is coordinated to  $\text{Ni}^{\text{II}}$ .

**Solution Structure of the Binuclear Calixsalen Complexes.** The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the diamagnetic binuclear  $\text{Ni}^{\text{II}}$  complexes **4a** and **4b** were much simpler. The observation of half the number resonances as were found in the mononuclear analogues requires a more symmetrical, binuclear complex. For example, only two imine proton signals and four metaphenolic proton resonances were observed for **4a** and **4b**.  $^{13}\text{C}$  NMR showed 2 imine, 12 aromatic, 1 bridging methylene, and 2 cyclohexane diamine CHN carbon resonances.

$C_2$  symmetry permits two conformers, either syn or anti with respect to the two salen sites. Examination of the  $^1\text{H}$  NMR spectra revealed that the two bridging methylene protons are diastereotopic, appearing as AB doublets. Therefore, a syn conformation in which the  $C_2$  axis is orthogonal to a line connecting the two chemically equivalent bridging methylene groups is required.

The binuclear  $\text{Ni}^{\text{II}}$  complex **5** was very sparingly soluble in common organic solvents, and hence only  $^1\text{H}$  NMR data could be obtained. The presence of a  $C_2$  axis was established by the observation of two doublets assigned to nonequivalent coordinated imine protons at 5.90 and 5.79 ppm (cf. Experimental). Reinhoudt<sup>5,47,48</sup> has reported numerous examples of related crown-ether, disalen macrocycles in which two salen units are joined by ethylene glycol or poly(ethylene glycol) links at the salen 3,3'- rather than the 5,5'-positions. In the solid state these molecules are invariably syn folded. It was not possible to establish conformation in the case of **5** on the basis of NMR evidence.

**Solid-State Structure of 4b and 5.** The solid-state structures of complexes **4b** and **5** were determined by X-ray crystallography to determine conformation, cavity shape and size, and the Ni–Ni distances.<sup>10,24,49</sup> Dark-red crystals of **4b** and **5** were grown by slow evaporation of  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2/\text{EtOH}$  solutions. The molecular structures obtained from X-ray diffraction studies are shown in Figures 3 and 4.

In the solid state, the structure of the disalen macrocycle **4b**· $\text{CH}_3\text{CN}$  (Figure 3) is approximately  $C_2$  symmetric, as inferred from solution NMR experiments. The coordination geometry of both  $\text{Ni}^{\text{II}}$  atoms is distorted square planar, with bond angles approximating those of its mononuclear analogue **3b**. The  $\text{Ni}^{\text{II}}$ -donor atom distances were typical for  $\text{Ni}^{\text{II}}$ –salen complexes.<sup>46</sup> As shown in Figure 3, the solution conformation is maintained in the solid state, and the molecule folds in a syn fashion on an axis passing through the two methylene linking groups. The two coordinated salen sites lie approximately cofacial; however, because of angle strain of the joining methylene groups on the **4b** fold axis, the Ni–Ni separation is very large at 7.15 Å. We note that Whiting<sup>50</sup> reported a related 1,8-naphthyl linked disalen macrocycle with a presumed anti fold which was later<sup>51</sup> shown to be more consistent with a syn folded structure very similar to that of **4b**. The metal–metal separation in Reinhoudt's syn-folded crown ether disalens, in which the salen units are joined by flexible links, settles at ca. 3.5 Å,<sup>48</sup> a distance probably determined by  $\pi$ -stacking interactions. The short, rigid methylene links of **4b** result in considerable angle strain, which is distributed throughout the ring to minimize energy. For example, a relatively small angle deformation to 106.5° results for the  $\text{sp}^3$  linking carbons C21 and C42. All four benzene rings are slightly boat-shaped, with average hinge angles ( $\alpha$ ) of 5.6° for the connection to the methylene link and 10.3° for the connection to the salen oxygen. Average bending ( $\beta$ ) of the bond from the ipso carbon to the oxygen or imine carbon, as measured by the dihedral between the ipso bond and the plane

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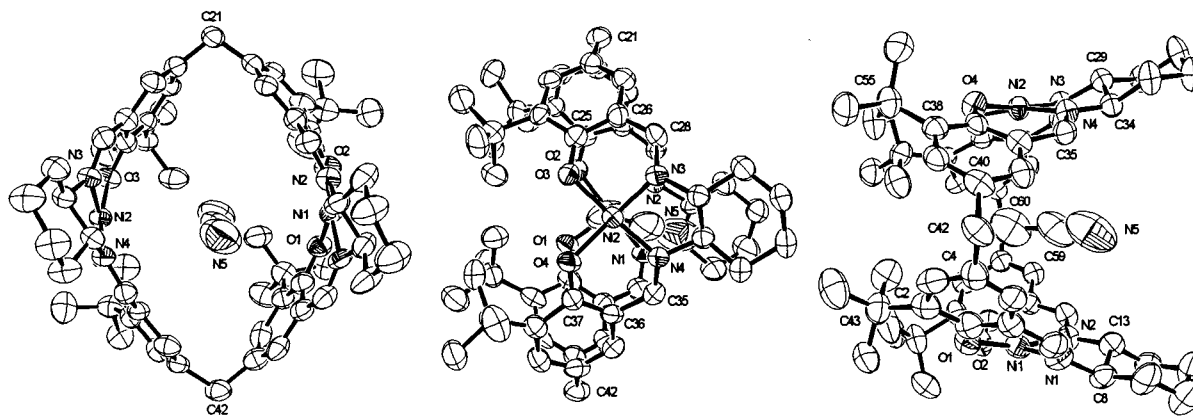


Figure 3. Views of ORTEP representations of the molecular structure of **4b** showing CH<sub>3</sub>CN guest.

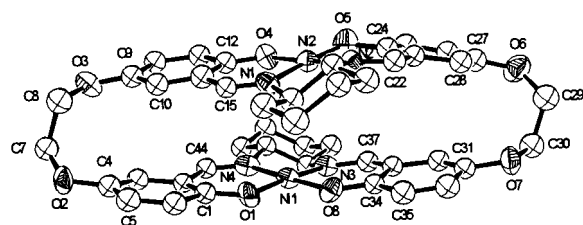


Figure 4. ORTEP representation of the dinickel complex **5**.

defined by C<sub>ipso</sub> and both C<sub>ortho</sub> atoms, is relatively small at 3.0 and 4.5°. A more significant average  $\beta$  deformation of 11.4° occurs at the C<sub>ipso</sub> connected to the methylene carbon. Coordination around the Ni atoms is also significantly distorted from square planar. The average dihedral angles between the two Ni–O–N planes is 13.7°.

The four salen benzene rings in macrocycle **4b** establish an oval-shaped cavity, cf. Figure 3, defined by the C<sub>21</sub>–C<sub>42</sub> distance of 11.3 Å and the Ni<sub>1</sub>–Ni<sub>2</sub> distance of 7.2 Å. Figure 3 shows that entrance to the cavity via the *tert*-butyl substituted side is effectively precluded by the small aperture resulting from a relatively close H–H distance of ca. 2.7 Å. The *tert*-butyl groups effectively form a gate which limits entrance of guests to the cyclohexyl side of **4b**. In the solid state, the dinickel complex **4a** contains a guest acetonitrile molecule in the cavity, with the methyl group lying approximately midway between the two Ni<sup>II</sup> atoms and the –C≡N group projecting into the space between the cyclohexane rings. This guest orientation suggests that the acetonitrile molecule approaches the cavity from the cyclohexane side. Furthermore, the distances between the CH<sub>3</sub>CN hydrogens and the carbons in the nearby benzene rings ranged from 2.7 to 3.9 Å. Thus, H/ $\pi$  interactions<sup>52,53</sup> within the electron-rich, aromatic cavity, rather than coordination of –C≡N to Ni<sup>II</sup>, likely drive the supramolecular host–guest interaction. A similar inclusion compound between *p*-*tert*-butylcalix[4]arene tetracarboxylate and acetonitrile has been structurally characterized.<sup>54</sup>

Similar to the dinickel complex **4b**, the salen units in complex **5** also adopted a parallel, cofacial conformation (Figure 4). However, unlike the strained salen units in complex **4b**, which were distorted from planarity, the salen units in the more flexible complex **5** are approximately planar. More interestingly, the solid-state conformation of **5** prefers an anti arrangement of the two cyclohexyl rings. Owing to the flexible ethylene glycol linking groups,  $\pi$ -stacking interactions fix a Ni–Ni distance of ca. 3.72 Å for the resultant cofacial salen groups, very similar to Reinhoudt's syn-folded crown ether disalens<sup>48</sup> or the [Mo<sub>2</sub>O<sub>5</sub>]<sup>2+</sup>-bridged disalen reported by Coucouvanis.<sup>19</sup>

**Summary.** Solvent-controlled coordination of chiral disalen macrocycles with Ni<sup>II</sup> salts afforded mono- and binuclear complexes. Solution and solid-state structural characterization shows that the macrocycles maintain a molecular-sized cavity. host–guest properties have been demonstrated in solution for the mononuclear nickel complex **3b** and in the solid state for its binuclear nickel analogue **4b**. The chiral dinickel complexes were structurally unique in that the cavity size and shape, as well as the Ni–Ni distance, were determined by the salen linking groups. These results will be useful in further design of bimetallic, macrocyclic chiral hosts for chiral recognition, asymmetric catalysis, and biomimetic studies.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determinations of **3b**, **4b**, and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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