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Synthesis and Characterization of Chiral Tetraaza Macrocyclic Nickel(II) and Palladium(II) Complexes

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Chiral tetraaza macrocyclic nickel(II) and palladium(II) complexes **2a**–**e**, containing one or two (*R,R*)-(–)-1,2-cyclohexanediyl bridges, were synthesized by template condensation reactions and characterized by ^{1}H and ^{13}C NMR, IR, UV–vis, and mass spectrometry. The electrophilic reactivity of **2a** was explored. Crystal structures of Ni complex **2b** and metal-free ligand **5** were determined by single-crystal X-ray diffraction.

Introduction

The design and preparation of tetraaza macrocyclic ligands and their transition metal complexes has long been a field of extensive investigation. The initial interest in these compounds derived from their potential as small-molecule analogues of the active sites of hemoproteins and metalloenzymes. The class of tetraaza macrocycles first reported by Jäger[1] was well studied by changing the ring size, the peripheral substituents, and the central metals.[2] Metal complexes of these ligands were investigated in catalytic electrochemical reduction of carbon dioxide[3] and for the activation of dioxygen.[4] Further work by Busch provided a new series of lacunar cyclidene complexes that showed remarkable dioxygen affinity.[5] Rational design and fine-tuning led to successful non-porphyrin oxygen carriers. These complexes were also used as oxygenation catalysts with molecular dioxygen[6] and as hosts for the formation of inclusion complexes.[7]

Chiral side chains have been introduced at the *meso* positions of this class of tetraaza macrocyclic complexes.[8] However, tetraaza macrocyclic complexes in this family bearing chiral bridges have not been reported. This is surprising, considering their possible application in asymmetric catalysis and the potentially strong analogy to the highly successful asymmetric tetradentate salen ligands developed and utilized by Jacobsen[9] and others.[10] We set out to incorporate chiral diamine bridges into new macrocyclic tetraazatetraene (TATE) ligands. Herein, we report the synthesis and characterization of a series of new chiral TATE Ni(II) and Pd(II) complexes and reactivity toward electrophilic substitution.

Experimental Section

Materials and Instrumentation. (1*R*,2*R*′)-[3,3′-[1,2-cyclohexanediylbis(iminomethylidyne)]bis[2,4-pentanedionato](2−)-$N,N',O^2,O^{2'}$]nickel(II) (**1a**) and [3,3′-[ethylenebis(iminomethylidyne)]-bis[2,4-pentanedionato](2−)-$N,N',O^2,O^{2'}$]nickel(II) (**1b**) were synthesized as reported.[11] (*R,R*)-(−)-1,2-diaminocyclohexane (dach) was resolved from a commercial mixture by a published procedure of Jacobsen.[12] All other reagents were used as purchased.

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^1H and ^{13}C NMR data were acquired on Varian VXR (300 MHz, 20 °C) or Bruker DRX (400 MHz, 25 °C) spectrometers. Chemical shifts are referenced to proton solvent impurities (δ 7.24, $CDCl_3$; δ 1.94, CD_3CN). UV−vis data were recorded on a HP8453A diode array spectrophotometer and reported as λ_{max} in nanometers (log ϵ). Fourier transform infrared spectra were recorded on a FT-DL spectrometer. For mass spectra, a Finnegan TSQ 700 spectrometer equipped with EI or ESI ion sources was used. Elemental analyses (C, H, N) were performed by Iowa State University Instrument Services.

Synthesis of Ni[cp-TATE(Ac)$_2$]^{13} (2a). A slurry of **1a** (1.02 g, 1.51 mmol) in 1,3-diaminopropane (ca. 8 mL) was refluxed under N_2 for 2 h, in which period all the solid dissolved and the color changed from orange to red. Water (10 mL) was added after cooling. The resulting precipitate was collected by filtration, washed with water, methanol, and diethyl ether, and dried in air to give a pure, red product. Yield: 0.97 g (86%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.46 (s, 2H, vinyl-*H*), 3.64 (m, 2H, $NCH_2CH_2CH_2N$), 3.56 (m, 2H, $NCH_2CH_2CH_2N$), 2.64 (m, 2H, C_6H_{10}), 2.39 (s, 6H, CH_3), 2.25 (s, 6H, $COCH_3$), 2.21 (m, 2H, C_6H_{10}), 1.89 (m, 2H, C_6H_{10}), 1.78 (m, 2H, $NCH_2CH_2CH_2N$), 1.29 (m, 2H, C_6H_{10}), 1.26 (m, 2H, C_6H_{10}). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 194.2 ($COCH_3$), 167.7 (vinyl-*C*), 152.1 (vinyl-*C*), 113.3 (vinyl-*C*), 70.1 (*c*-C_6H_{10}), 45.8 ($NCH_2CH_2CH_2N$), 29.5 (*c*-C_6H_{10}), 28.4 ($COCH_3$), 27.0 ($NCH_2CH_2CH_2N$), 25.4 (*c*-C_6H_{10}), 18.8 (CH_3). IR (KBr): 2926, 1629, 1578, 1511, 1395, 1293, 1275 cm^{-1}. UV−vis (CH_2Cl_2): 331 (4.75). MS (ESI): *m/z* 429 (M^+). Anal. Found: C, 58.63; H, 7.26; N, 13.14. Calcd for $C_{21}H_{30}N_4O_2Ni$: C, 58.77; H, 7.05; N, 13.05.

Synthesis of Ni[cc-TATE(Ac)$_2$] (2b). A mixture of **1a** (98.2 mg, 0.251 mmol) and (*R*,*R*)-1,2-diaminocyclohexane (ca. 1.0 g) was refluxed under N_2 for 6 h, in which period all the solid dissolved and the color changed from orange to red. Water (ca. 3 mL) was added after cooling. The crude product was collected by filtration and purified by chromatography (EtOAc/silica gel, 1 cm × 25 cm column). The product was redissolved in CH_2Cl_2 (ca. 3 mL) and layered with Et_2O (ca. 3 mL) to produce dark red prisms. Yield: 47 mg (40%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.56 (s, 2H, vinyl-*H*), 3.61 (m, 2H, C_6H_{10}), 2.73 (m, 2H, C_6H_{10}), 2.47 (s, 6H, CH_3), 2.43 (m, 2H, C_6H_{10}), 2.27 (m, 2H, C_6H_{10}), 2.22 (s, 6H, $COCH_3$), 1.86 (m, 2H, C_6H_{10}), 1.71 (m, 2H, C_6H_{10}), 1.31 (m, 8H, C_6H_{10}). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 193.7 ($COCH_3$), 170.8 (vinyl-*C*), 153.7 (vinyl-*C*), 114.7 (vinyl-*C*), 72.3 (*c*-C_6H_{10}), 69.2 (*c*-C_6H_{10}), 34.5 (*c*-C_6H_{10}), 29.9 (*c*-C_6H_{10}), 29.0 ($COCH_3$), 25.6 (*c*-C_6H_{10}), 25.1 (*c*-C_6H_{10}), 25.0 (CH_3). IR (KBr): 2935, 1577, 1560, 1296 cm^{-1}. UV−vis (CH_2Cl_2): 334 (4.55). MS (ESI): *m/z* 469 (M^+). Anal. Found: C, 61.21; H, 7.09; N, 12.00. Calcd for $C_{24}H_{34}N_4O_2Ni$: C, 61.43; H, 7.30; N, 11.94.

Synthesis of Ni[ec-TATE(Ac)$_2$] (2c). The procedure for **2a** was followed, starting from **1b** (3.18 g, 9.45 mmol) and excess (*R*,*R*)-1,2-diaminocyclohexane (ca. 16 mL). Recrystallization by layering a $CHCl_3$ (ca. 15 mL) solution with MeOH (ca. 10 mL) afforded an analytically pure purple product. Yield: 1.61 g (41%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.58 (s, 2H, vinyl-*H*), 3.60 (m, 2H, C_6H_{10}), 3.26 (m, 2H, NCH_2CH_2N), 3.08 (m, 2H, NCH_2CH_2N), 2.46 (s, 6H, CH_3), 2.43 (m, 2H, C_6H_{10}), 2.22 (s, 6H, $COCH_3$), 1.72 (m, 2H, C_6H_{10}), 1.32 (m, 4H, C_6H_{10}). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 193.9 ($COCH_3$), 171.3 (vinyl-*C*), 157.9 (vinyl-*C*), 114.7 (vinyl-*C*), 72.8 (NCH_2CH_2N), 57.9 (*c*-C_6H_{10}), 34.8 (*c*-C_6H_{10}), 29.2 ($COCH_3$), 25.9 (*c*-C_6H_{10}), 25.5 (CH_3). IR (KBr): 2937, 2857, 1578, 1399, 1367, 1287 cm^{-1}. UV−vis (CH_2Cl_2): 336 (4.62). MS (ESI): *m/z* 415 (M^+). Anal. Found: C, 57.76; H, 6.81; N, 13.28. Calcd for $C_{20}H_{28}N_4O_2Ni$: C, 57.86; H, 6.80; N, 13.50.

Synthesis of Pd[ce-TATE(Ac)$_2$] (2d). The precursor **1c** was synthesized in a manner similar to its nickel analogue, from free ligand (1*R*,2*R*′)-3,3′-[1,2-cyclohexanediylbis(iminomethylidyne)]-bis[2,4-pentanedione]^{11a} (104 mg, 0.311 mmol) and $Pd(OAc)_2$ (72 mg, 0.321 mmol) in a refluxing methanolic solution (ca. 6 mL). Yield: 90 mg (67%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.78 (s, 2H, $C{=}CHN$), 3.31 (m, 2H, NCH), 2.52 (s, 8 H, CH_3 and C_6H_{10}), 2.33 (s, 6H, CH_3), 1.93 (m, 2H, C_6H_{10}), 1.44 (m, 2H, C_6H_{10}), 1.35 (m, 2H, C_6H_{10}).

A slurry of **1c** (43 mg, 0.098 mmol) in ethylenediamine (ca. 1 mL) was refluxed under N_2 for 1 h. Addition of 10 mL of water led to a yellow precipitate, which was collected and recrystallized by layering a CH_2Cl_2 (ca. 2 mL) solution with Et_2O (ca. 2 mL). Yield: 34 mg (74%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.98 (s, 2H, vinyl-*H*), 3.68 (m, 4H, NCH_2CH_2N), 3.34 (m, 2H, C_6H_{10}), 2.53 (m, 2H, C_6H_{10}), 2.40 (s, 6H, CH_3), 2.33 (s, 6H, $COCH_3$), 1.93 (m, 2H, C_6H_{10}), 1.41 (m, 4H, C_6H_{10}). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 195.8 ($COCH_3$), 165.0 (vinyl-*C*), 150.9 (vinyl-*C*), 113.2 (vinyl-*C*), 73.1 (*c*-C_6H_{10}), 56.3 (NCH_2CH_2N), 29.6 ($COCH_3$), 28.7 (*c*-C_6H_{10}), 25.1 (*c*-C_6H_{10}), 20.6 (CH_3). IR (KBr): 2932, 2857, 1576, 1559, 1332, 1272 cm^{-1}. UV−vis (CH_2Cl_2): 311 (4.35). MS (EI): *m/z* 461 (M^+).

Synthesis of Pd[cp-TATE(Ac)$_2$] (2e). A slurry of **1c** (45 mg, 0.103 mmol) in 1,3-diaminopropane (ca. 1 mL) was refluxed under N_2 for 1 h. Addition of 10 mL of water led to a yellow precipitate, which was collected and recrystallized by layering a CH_2Cl_2 (ca. 2 mL) solution with Et_2O (ca. 2 mL). Yield: 36 mg (73%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.74 (s, 2H, vinyl-*H*), 3.40 (m, 2H, $NCH_2CH_2CH_2N$), 3.31 (m, 2H, $NCH_2CH_2CH_2N$), 3.23 (m, 2H, C_6H_{10}), 2.39 (s, 6H, CH_3), 2.31 (m, 2H, C_6H_{10}), 2.25 (s, 6H, $COCH_3$), 2.17 (m, 2H, $NCH_2CH_2CH_2N$), 1.90 (m, 2H, C_6H_{10}), 1.42 (m, 2H, C_6H_{10}), 1.34 (m, 2H, C_6H_{10}). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 194.8 ($COCH_3$), 167.2 (vinyl-*C*), 152.0 (vinyl-*C*), 112.9 (vinyl-*C*), 72.3 (*c*-C_6H_{10}), 51.7 ($NCH_2CH_2CH_2N$), 33.2 (*c*-C_6H_{10}), 30.1 ($NCH_2CH_2CH_2N$), 28.8 ($COCH_3$), 25.4 (*c*-C_6H_{10}), 21.8 (CH_3). IR (KBr): 2926, 2859, 1576, 1394, 1294, 1278 cm^{-1}. UV−vis (CH_2Cl_2): 315 (4.74) MS (ESI): *m/z* 476 (M^+). Anal. Found: C, 51.29; H, 6.82; N, 11.39. Calcd for $C_{21}H_{30}N_4O_2Pd$: C, 52.89; H, 6.34; N, 11.75.

Synthesis of Ni[cp-TATE(NO$_2$)$_2$] (3a). To a suspension of **2a** (202 mg, 0.472 mmol) in CH_3CN (ca. 10 mL) was added $NaNO_2$ (98 mg, 1.42 mmol) and CF_3COOH (180 mg, 1.58 mmol) at room temperature. The darkened mixture was stirred overnight and filtered. The solid was recrystallized by layering a $CHCl_3$ (ca. 4 mL) solution with Et_2O (ca. 4 mL) to provide red needles of **3a**. Yield: 153 mg (74%). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.20 (s, 2H, vinyl-*H*), 3.72 (m, 4H, $NCH_2CH_2CH_2N$), 2.69 (m, 2H, C_6H_{10}), 2.47 (s, 6H, CH_3), 2.28 (m, 2H, C_6H_{10}), 1.90 (m, 2H, C_6H_{10}), 1.84 (m, 2H, $NCH_2CH_2CH_2N$), 1.44 (m, 2H, C_6H_{10}), 1.24 (m, 2H, C_6H_{10}). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 165.2 (vinyl-*C*), 151.3 (vinyl-*C*), 129.6 (vinyl-*C*), 70.5 (*c*-C_6H_{10}), 46.4 ($NCH_2CH_2CH_2N$), 29.5 (*c*-C_6H_{10}), 26.4 ($NCH_2CH_2CH_2N$), 25.0 (*c*-C_6H_{10}), 18.6 (CH_3). IR (KBr): 2931, 2866, 1613, 1481, 1306, 1269, 1234, 1166 cm^{-1}. UV−vis (CH_2Cl_2): 413 (4.84). MS (EI): *m/z* 434 (M^+). Anal. Found: C, 46.89; H, 5.70; N, 19.36. Calcd for $C_{17}H_{24}N_6O_4Ni$: C, 46.93; H, 5.56; N, 19.31.

Synthesis of Ni[cp-TATE(Ac)(NO$_2$)] (3b). To a suspension of **2a** (103.2 mg, 0.240 mmol) in CH_3CN (ca. 5 mL) was added $NaNO_2$ (17.2 mg, 0.249 mmol) and CF_3COOH (27.5 mg, 0.241 mmol) at room temperature. The mixture was stirred for 4 h and filtered. The solid was recrystallized by layering a CH_2Cl_2 (ca. 3 mL) solution with Et_2O (ca. 3 mL) to provide an orange product.

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(13) The first and second lower case letters in the ligand acronym refer to the type of A and B bridges in Scheme 1, respectively (e = 1,2-ethyl, c = (*R*,*R*)-1,2-cyclohexanediyl, and p = 1,3-propyl).

Yield: 35 mg (40%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.25 (s, 1H, vinyl-*H*), 7.42 (s, 1H, vinyl-*H*), 3.69 (m, 3H, NC*H*$_2$CH$_2$C*H*$_2$N), 3.53 (m, 1H, NC*H*$_2$CH$_2$C*H*$_2$N), 2.67 (m, 2H, C$_6$*H*$_{10}$), 2.45 (s, 3H, C*H*$_3$), 2.41 (s, 3H, C*H*$_3$), 2.26 (s, 3H, COC*H*$_3$), 2.21 (m, 2H, C$_6$*H*$_{10}$), 1.89 (m, 2H, C$_6$*H*$_{10}$), 1.82 (m, 2H, NCH$_2$C*H*$_2$CH$_2$N), 1.40 (m, 2H, C$_6$*H*$_{10}$), 1.26 (m, 2H, C$_6$*H*$_{10}$). ^{13}C NMR (CDCl$_3$, 300 MHz): δ 194.4 (*C*OCH$_3$), 167.7 (vinyl-*C*), 164.9 (vinyl-*C*), 151.8 (vinyl-*C*), 151.2 (vinyl-*C*), 129.0 (vinyl-*C*), 113.3 (vinyl-*C*), 70.6 (*c*-C$_6$H$_{10}$), 69.7 (*c*-C$_6$H$_{10}$), 46.3 (N*C*H$_2$CH$_2$*C*H$_2$N), 45.5 (N*C*H$_2$CH$_2$*C*H$_2$N), 29.6 (*c*-C$_6$H$_{10}$), 29.1 (*c*-C$_6$H$_{10}$), 28.3 (NCH$_2$*C*H$_2$CH$_2$N), 26.4 (*c*-C$_6$H$_{10}$), 25.0 (*c*-C$_6$H$_{10}$), 18.53 (*C*H$_3$), 18.49 (*C*H$_3$),. IR (KBr): 2931, 1584, 1560, 1274, 1240, 1003 cm^{-1}. UV−vis (CH$_2$Cl$_2$): 403 (4.65). MS (EI): *m*/*z* 431 (M$^+$).

Synthesis of Ni[cp-TATE(H)$_2$]·2HPF$_6$ (4). To a suspension of **2a** (206 mg, 0.480 mmol) in hot water (3 mL) was added 1 mL of HCl (concentrated). After all the solid dissolved, NH$_4$PF$_6$ (158 mg, 0.971 mmol) was added to give a yellow precipitate **4**, which was filtered out, washed with cold water and Et$_2$O, and air-dried. Yield: 247 mg (89%). ^{1}H NMR (CD$_3$CN, 300 MHz): δ 4.37 (br s, 2H), 4.11 (br s, 2H), 3.77 (m, 4H), 3.21 (s, 2H), 2.17 (s, 2H), 2.07 (s, 6H), 1.97 (m, 2H), 1.81 (m, 2H), 1.33 (m, 4H). ^{13}C NMR (CD$_3$CN, 300 MHz): δ 179.8, 165.7, 119.8, 70.9, 48.4, 48.3, 30.6, 24.7, 24.0. IR (KBr): 2945, 2864, 1684, 1559, 1540, 1456, 837, 558 cm^{-1}. UV−vis (CD$_3$CN): 290 (3.32). MS (ESI): *m*/*z* 491 (M$^+$ − HPF$_6$), 345 (M$^+$ − 2HPF$_6$). Anal. Found: C, 31.51; H, 4.38; N, 8.58. Calcd for C$_{17}$H$_{28}$N$_4$P$_2$F$_{12}$Ni: C, 32.05; H, 4.43; N 8.79.

Synthesis of H$_2$[cp-TATE]·2HPF$_6$ (5). Hydrogen chloride gas was bubbled through a solution of **4** (137.5 mg, 0.217 mmol) in absolute ethanol (5 mL) until it turned blue. Solvent was removed in vacuo and the residue dissolved in water (1 mL). After addition of NH$_4$PF$_6$ (120 mg, 0.736 mmol), the mixture was cooled in a refrigerator to 0 °C for 6 h. The colorless crystalline product **5** was filtered out and washed by water and diethyl ether. Yield: 115.2 mg (91%). ^{1}H NMR (CD$_3$CN, 300 MHz): δ 7.85 (m, δ vinyl), 7.66 (m, δ vinyl), 7.44 (m, δ vinyl), 7.25 (br m, N*H*), 6.90 (br m, N*H*), 5.39 (d, $J_{\mathrm{H-H}} = 12.3$ Hz, γ vinyl), 5.19 (d, $J_{\mathrm{H-H}} = 11.4$ Hz, γ vinyl), 5.11 (d, $J_{\mathrm{H-H}} = 12.0$ Hz, γ vinyl), 4.95 (d, $J_{\mathrm{H-H}} = 12.9$ Hz, γ vinyl), 3.1−3.7 (m, NC*H* on C$_6$H$_{12}$ and NC*H*$_2$), 2.32 (m, C*H*$_3$), 1.7−2.3 (m, C$_6$*H*$_{12}$), 1.2−1.6 (m, C$_6$*H*$_{12}$ and NCH$_2$C*H*$_2$-CH$_2$N). IR (KBr): 3386, 3363, 3226, 3.69, 2946, 1636, 841, 559 cm^{-1}. Anal. Found: C, 35.17; H, 5.44; N, 9.56. Calcd for C$_{17}$H$_{30}$N$_4$P$_2$F$_{12}$: C, 35.18; H, 5.21; N, 9.65.

X-ray Crystallography. Single-crystal intensity data collections for **2b** and **5** were performed on a Bruker SMART 1000 CCD-based diffractometer with graphite-monochromated Mo Kα radiation (0.710 73 Å), using the full-sphere $\omega/2\theta$ scan routine. The datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiply equivalent measurements.[14] Details about crystal data, data collection, and structure solution and refinement are summarized in Table 1. Selected bond distances and bond angels are collected in Tables 2 and 3 for compounds **2b** and **5**, respectively.

Table 1. Crystal and Structure Refinement Data for **2b** and **5**

	2b	**5**
formula	C$_{24}$H$_{34}$N$_4$NiO$_2$	C$_{17}$H$_{30}$F$_{12}$N$_4$P$_2$
fw	469.26	580.39
cryst size (mm^3)	0.3 × 0.2 × 0.2	0.4 × 0.2 × 0.1
temp (K)	298(2)	173(2)
cryst system	triclinic	orthorhombic
space group	$P1$	$C222_1$
a (Å)	9.9537(8)	13.3960(16)
b (Å)	10.9729(8)	14.9412(18)
c (Å)	11.8826(9)	12.0953(14)
α (deg)	67.3100(10)	90
β (deg)	75.226(2)	90
γ (deg)	68.5490(10)	90
V (Å^3)	1104.59(15)	2420.9(5)
Z	2	4
D_{calc} (Mg/m^3)	1.411	1.592
abs coeff (mm^{-1})	0.907	0.286
F(000)	500	1192
θ range (deg)	2.11−28.25	2.04−24.72
reflcns collcd	9155	6229
indpdt reflcns	6732 [R(int) = 0.0286]	2072 [R(int) = 0.0312]
max and min transm	1 and 0.71	0.81 and 0.75
refinement method on F^2	full-matrix least squares	full-matrix least squares
data/restraints/params	6732/3/568	2072/0/219
goodness-of-fit on F^2	0.983	0.972
final R indices [$I > 2\sigma(I)$]	R1 = 0.0352, wR2 = 0.0837	R1 = 0.0335, wR2 = 0.0778
R indices (all data)	R1 = 0.0407, wR2 = 0.0860	R1 = 0.0428, wR2 = 0.0807

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2b**

Ni(1A)−N(2A)	1.852(4)	C(1A)−C(3A)	1.434(6)
Ni(1A)−N(3A)	1.855(3)	C(3A)−C(6A)	1.411(6)
Ni(1A)−N(4A)	1.868(3)	C(6A)−N(2A)	1.307(6)
Ni(1A)−N(1A)	1.917(3)	C(7A)−N(2A)	1.495(5)
C(1A)−N(1A)	1.321(5)	C(12A)−N(3A)	1.480(6)
N(3A)−Ni(1A)−N(2A)	85.44(16)	N(4A)−Ni(1A)−N(1A)	89.11(15)
N(3A)−Ni(1A)−N(4A)	92.13(15)	N(2A)−Ni(1A)−N(4A)	173.75(14)
N(2A)−Ni(1A)−N(1A)	93.81(15)	N(3A)−Ni(1A)−N(1A)	174.84(16)

Table 3. Bond Lengths (Å) and Angles (deg) for **5**[a]

C(1)−C(1)$^{\#1}$	1.518(5)	C(5)−C(7)	1.395(3)
C(1)−C(2)	1.527(4)	C(6)−C(7)	1.499(4)
C(2)−C(3)	1.521(3)	C(7)−N(2)	1.310(3)
C(3)−N(1)	1.458(3)	C(8)−N(2)	1.455(3)
C(3)−C(3)$^{\#1}$	1.548(5)	C(8)−C(9)	1.515(3)
C(4)−N(1)	1.324(3)	C(9)−C(8)$^{\#1}$	1.515(3)
C(4)−C(5)	1.365(4)		
C(1)$^{\#1}$−C(1)−C(2)	112.3(2)	N(2)−C(7)−C(5)	123.0(2)
C(3)−C(2)−C(1)	109.8(2)	N(2)−C(7)−C(6)	114.8(2)
N(1)−C(3)−C(2)	114.0(2)	C(5)−C(7)−C(6)	122.2(2)
N(1)−C(3)−C(3)$^{\#1}$	109.87(16)	N(2)−C(8)−C(9)	111.2(2)
C(2)−C(3)−C(3)$^{\#1}$	109.53(18)	C(8)−C(9)−C(8)$^{\#1}$	114.8(3)
N(1)−C(4)−C(5)	127.3(2)	C(4)−N(1)−C(3)	121.6(2)
C(4)−C(5)−C(7)	121.1(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1, x, $-y + 1$, $-z + 2$.

A black prism of **2b** was selected for X-ray analysis. The systematic absences in the diffraction data were consistent for the space groups $P1$ and $P\bar{1}$. The *E*-statistics strongly suggested the noncentrosymmetric space group yielding chemically reasonable and computationally stable results of refinement. The positions of Ni atoms were found by the Patterson method. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps and were refined in full-matrix anisotropic approximation. All hydrogen atoms were placed at calculated positions and refined using a riding model. All attempts to transform the atomic coordinates to satisfy centrosymmetric space group $P\bar{1}$ gave a model with strong disorder in six-membered rings and unreasonable thermal ellipsoids for the remaining atoms.

A thin colorless plate of **5** was used for X-ray analysis. The positions of all non-hydrogen atoms were found by direct methods and refined with a full-matrix anisotropic approximation. The hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps and were refined using a riding model.

Results and Discussion

Synthesis and Characterization of Macrocyclic Complexes. Macrocyclic ligands can be synthesized by a wide

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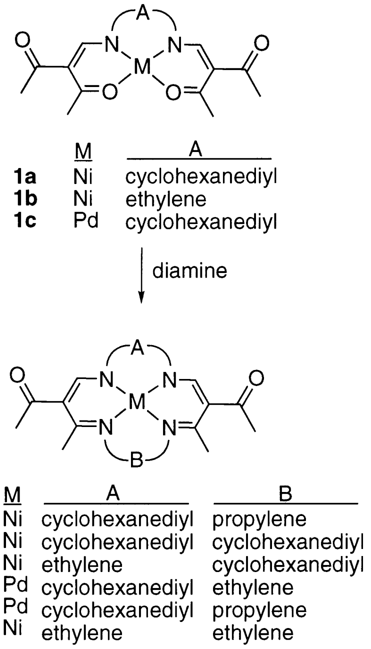
(14) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.

Scheme 1. Synthesis of Macrocyclic Complexes



	M	A
1a	Ni	cyclohexanediyl
1b	Ni	ethylene
1c	Pd	cyclohexanediyl

	M	A	B
2a	Ni	cyclohexanediyl	propylene
2b	Ni	cyclohexanediyl	cyclohexanediyl
2c	Ni	ethylene	cyclohexanediyl
2d	Pd	cyclohexanediyl	ethylene
2e	Pd	cyclohexanediyl	propylene
2f	Ni	ethylene	ethylene

variety of methods, among which template synthesis[15] is one of the most widely used strategies. Here, macrocyclic tetraazatetraene (TATE) complexes were prepared by template condensation of open-chain complexes with appropriate neat diamines with good to high yields in manner analogous to that previously reported. Thus, the reaction of **1a**,**b** with diamines yielded the corresponding macrocyclic tetraazatetraene complexes **2a**−**c** with one or two chiral cyclohexanediyl bridges incorporated (Scheme 1). The palladium complex **1c** also reacted readily with ethylenediamine or trimethylenediamine to afford **2d**,**e**, respectively.

The reaction between **1a** and ethylenediamine led to the formation of a double-ethylene-bridged product, Ni[ee-TATE(Ac)$_2$] (**2f**), presumably by a diamine exchange reaction. A similar exchange reaction was reported earlier.[2b] It was interesting to note that when the template cation Pd^{2+} was used under the same conditions, cyclization product Pd[ce-TATE(Ac)$_2$] (**2d**) was formed without further amine exchange. Although the reaction of **1a** with (*R*,*R*)-dach went smoothly to afford Ni[cc-TATE(Ac)$_2$] (**2b**), reaction of the palladium analogue **1c** with (*R*,*R*)-dach resulted in the decomposition of the ligand skeleton, and products were not further identified. Attempts to carry out the reaction in the presence of a solvent were unsuccessful.[16]

The identity and composition of the chiral macrocyclic tetraazatetraene Ni(II) and Pd(II) complexes were confirmed by elemental analyses as well as by electronic, infrared, and NMR spectroscopies and mass spectrometry. The assignment of the ^{1}H and ^{13}C signals in these complexes is based upon ^{13}C APT and 2D COSY (^{1}H/^{1}H) and HETCOR (^{1}H/^{13}C) NMR experiments. These data are consistent with square planar coordination around nickel and palladium centers. Generally, the imine protons appear around 7.4−8.2 ppm as a singlet. The protons associated with α carbons on bridge A (Scheme 1) appear at 2.6−3.3 ppm, while on bridge B these protons appear at a lower field, 3.4−3.7 ppm. Also, on incorporation of the chiral cyclohexyldiamine, the α protons on the trimethylene bridge of **2a** become nonequivalent. Four individual triplets were observed for these protons, although not completely baseline separated.

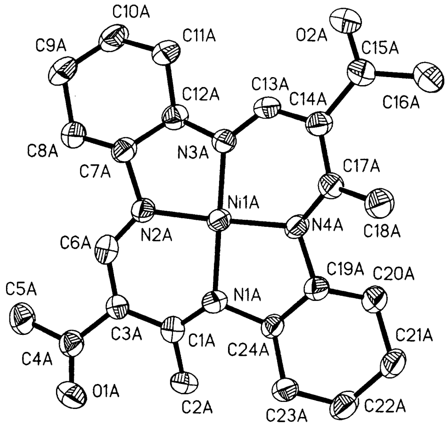


Figure 1. ORTEP of one of the two crystallographically independent molecules of **2b** at 50% probability level. Hydrogen atoms are omitted for clarity.

Structure of 2b. Two crystallographically nonequivalent molecules were found in the unit cell of **2b**. Both have very similar conformations (Figure 1) with Ni atoms placed almost in the plane of four N atoms (rms deviations are 0.071 and 0.085 Å). However, the 14-membered ring system is significantly distorted from a planar conformation (rms deviations are 0.190 and 0.208, respectively). Ni−N distances are of 1.845(4)−1.917(4) Å. N−C distances in 5- and 6-membered chelate rings range over 1.469(6)−1.498(6) and 1.285(6)−1.338(6) Å, respectively. Both molecules of **2b** in the asymmetric unit cell are almost parallel and form alternate layers in a crystal.

Some metrical correlations could be found in comparison with structures of (5,7,12,14-tetramethyldibenzo(*b*,*i*)-1,4,8,11-tetraaza-(14)-annulenato)nickel(II), Ni(TMTAA), and (6,13-diacetyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato-*N*,*N*′,*N*″,*N*‴)nickel(II), Ni[ee-TATE(Ac)$_2$]. Both crystallographically independent molecules in Ni(TMTAA) also have almost planar coordination of the Ni atoms.[17] However, the distortion of the 14-membered ring is much larger. The interplanar angle between these molecules is equal to 77.8°, forming a typical herringbone packing mode for the $P2_1/c$ space group. Half of the molecule of Ni[ee-TATE(Ac)$_2$] was found in the asymmetric unit of a monoclinic cell with the Ni atom in the inversion center.[18] The symmetry requirements led to rigorously planar coor-

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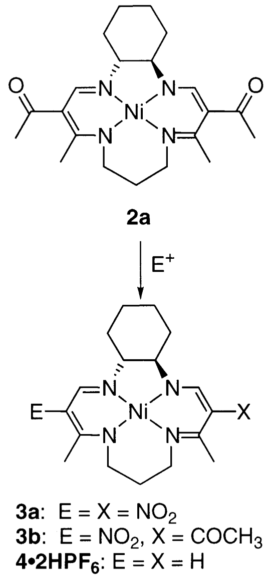
Scheme 2. Reactivity of **2a**



dination of Ni. However, the 14-membered ring is slightly distorted from planarity (rms deviations are 0.116 Å). All the molecules in the crystal of Ni[ee-TATE(Ac)$_2$] are parallel.

Reactivity toward Electrophiles. The *meso* (or γ) positions of 15-membered macrocyclic complexes of this type can undergo electrophilic substitutions.[19] As shown in Scheme 2, the reaction of **2a** with hydrochloric acid afforded the deacylated macrocyclic complex **4** as a yellow crystalline product. Compound **4** was unreactive to air in the solid state but turned black within days in solution on exposure to normal room atmosphere. Compound **2a** also reacted with nitrogen electrophiles. Treatment of **2a** with sodium nitrite and trifluoroacetic acid under oxidizing conditions resulted in the formation of mono- and dinitro complex **3a,b**, depending on the stoichiometry of the reaction.

Demetalation of **4** by gaseous hydrogen chloride produced a colorless crystalline product. Sharp IR peaks around 3386 and 3363 cm^{-1} indicated the presence of N−H functional groups. Satisfactory elemental analysis confirmed its composition as a metal-free ligand salt, **5**. However, the ^{1}H NMR spectrum of **5** was complicated. For example, there were four doublets around the γ vinyl region (4.9−5.5 ppm) with approximately equal intensity. At higher temperature (50 °C), these peaks, as well as all others, were slightly broadened but the relative intensity of these four doublets showed little change. Upon addition of D$_2$O, however, the ratio of these peaks changed considerably and broad peaks at 6.9 and 7.25 ppm disappeared. This suggested that more than one tautomeric forms of the ligand salt existed in solution.[20] Due to this complexity, the ^{13}C NMR spectrum of **5** was not clearly interpretable. However, three peaks at 93.2, 92.7, and 89.7 ppm can be assigned to the carbon resonances associated with γ vinyl protons. Attempts to obtain the pure, neutral ligand by deprotonation with various bases such as sodium acetate and sodium ethoxide were not successful. Nevertheless, the structure of **5** was finally established by an X-ray crystallographic analysis.

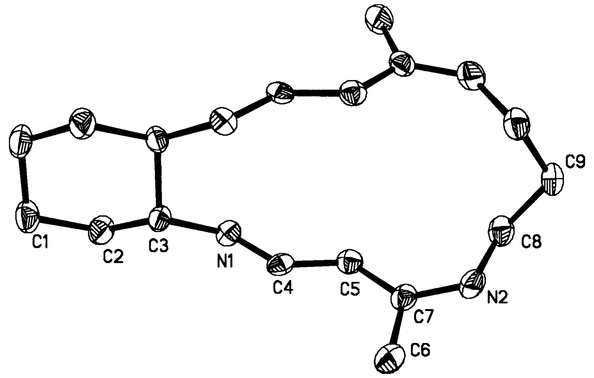


Figure 2. ORTEP of molecular structure of the [C$_{17}$H$_{30}$N$_4$]$^{2+}$ cation in **5**. H atoms are omitted for clarity.

Crystal Structure of 5. The asymmetric unit of **5** consists of half of the centrosymmetric cation [C$_{17}$H$_{30}$N$_4$]$^{2+}$ (Figure 2) and a PF$_6^-$ anion. The conformation adopted by **5** differs significantly from neutral tetraazaannulene analogues. For example, the bis(cyclohexanediyl)-bridged TATE macrocycle maintains a square planar arrangement of the four donor nitrogens in the solid state.[21] However, **5** has all four donor atoms protonated. The extra charge strongly disfavors the square planar arrangement of nitrogens. Only one of two N atoms takes part in cation−anion intermolecular interactions in structure of **5**.

Conclusion

In summary, we have shown that a series of chiral tetraaza macrocylic complexes can be readily prepared via template condensation reactions. The applications of these chiral tetraaza macrocyclic ligands and their complexes in asymmetric catalysis are underway.

Acknowledgment. We thank the Research Corp. for partial financial support.

Supporting Information Available: Tables giving crystallographic data for compounds **2b** and **5** including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters and ^{1}H NMR spectra for compounds **2a**−**c**, **3a**, and **5**. This information is available free of charge via the Internet at http://pubs.acs.org.

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