Inorg. Chem. **1998,** *37,* 6255−6262

Solid State and Solution Characterization of Chiral, Conformationally Mobile Tripodal Ligands

James W. Canary,*,[†] Craig S. Allen,[†] Jesus M. Castagnetto,[†] Yu-Hung Chiu,[†] Paul J. Toscano,[‡] and Yihan Wang[†]

Department of Chemistry, New York University, New York, New York 10003, and Department of Chemistry, SUNY Albany, Albany, New York 12222

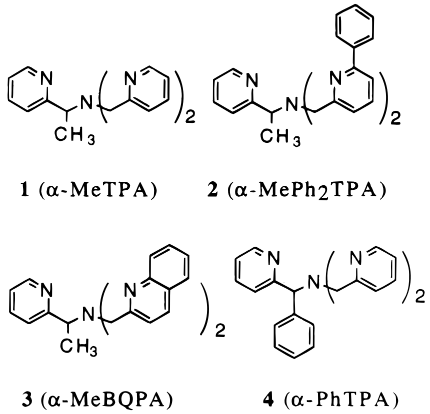
Received March 19, 1998

The synthesis of the ligands *N*,*N*-bis[(2-pyridyl)methyl]-1-(2-pyridyl)ethanamine (**1**, α-MeTPA), *N*,*N*-bis[(6-phenyl-2-pyridyl)methyl]-1-(2-pyridyl)ethanamine (**2**, α-MePh$_2$TPA), *N*,*N*-bis[(2-quinolyl)methyl]-1-(2-pyridyl)ethanamine, (**3**, α-MeBQPA), and *N*,*N*-bis[(2-pyridyl)]methyl(phenyl)(2-pyridyl)methanamine (**4**, α-PhTPA) is described. The ligands form chiral, pseudo C_3-symmetric complexes with Zn^{II} and Cu^{II} salts that possess an available electrophilic coordination site. X-ray crystallographic structures of the complexes [Zn(α-MeTPA)Cl](ClO$_4$), [Zn(α-MeBQPA)Cl](ClO$_4$), and [Zn(α-PhTPA)Cl](ClO$_4$) show that the spatial arrangement of the three pyridyl groups resembles a propeller whose directional sense is controlled by a substituent on one methylene arm. Chiroptical measurements provide supporting information that the complexes maintain similar structures in solution. Monte Carlo/stochastic dynamics (MC/SD) simulations of the [Zn(L)Cl]$^+$ complexes indicate that only two conformers are populated at normal temperatures, suggest the presence of a synchronicity in the movement of the heteroaromatic rings during conformer interconversions, and provide an estimate of the energy difference between the conformers.

Introduction

Chiral tripodal ligands related to tris(2-pyridylmethyl)amine (TPA, **1**) with an asymmetric center in one arm (e.g., α-MeTPA, **2**) have been used as chiral solvating agents for sulfoxides[1] and for metal ion sensing with multiple signals.[2] Copper(II) complexes of the ligands have been shown to display redox-switched chiroptical properties[3] and have been applied to the determination of absolute configurations of α-amino acids and *β*-amino alcohols.[4] These applications are possible as a result of subtle conformational properties of the ligand−metal complex. In this paper, we describe the synthesis, characterization and conformational analysis of Zn(II), Cu(II), and Cd(II) complexes of ligands **1**−**4** (Chart 1), which were the first compounds studied in this series of experiments.[1]

Chart 1



1 (α-MeTPA) **2** (α-MePh$_2$TPA)

3 (α-MeBQPA) **4** (α-PhTPA)

The solid-state structures of tetradentate TPA coordination complexes contain 5-, 6-, and 7-coordinate metal ions displaying several coordination geometries.[5−14] Two ligand conformations predominate:[7] the C_3 conformation (Figure 1a), in which a C_3 symmetry axis is present as exemplified by trigonal bipyramidal metal ion complexes of TPA; and the C_σ conformation (Figure 1c), in which a plane of symmetry is present as displayed by octahedral and square pyramidal metal−TPA complexes. As shown by the C_3 symmetric structure in Figure 1a, the ligand occupies four coordination sites with the tertiary amine in an axial position and the pyridyl nitrogens in three equatorial sites. An additional apical site (not shown) is available for solvent or anion coordination. Tetradentate TPA encompasses the metal ion with a spatial arrangement of the three pyridyl groups, tilting with respect to the metal−amine axis, which resembles a

---

[†] NYU.

[‡] SUNY Albany.

(1) Canary, J. W.; Allen, C. S.; Castagnetto, J. M.; Wang, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8484.

(2) Castagnetto, J. M.; Canary, J. W. *Chem. Commun.* **1998**, 203.

(3) Zahn, S.; Canary, J. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 305.

(4) Zahn, S.; Canary, J. W., manuscript submitted for publication.

(5) Dong, Y.; Fujii, H.; Hendrich, M. P.; Leising, R. A.; Pan, G.; Randall, C. R.; Wilkinson, E. C.; Zang, Y.; Que, L., Jr.; Fox, B. G.; Kauffmann, K.; Münck, E. *J. Am. Chem. Soc.* **1995**, *117*, 2778.

(6) Toftlund, H.; Larsen, S.; Murray, K. S. *Inorg. Chem.* **1991**, *30*, 3964.

(7) Allen, C. S.; Chuang, C.-L.; Cornebise, M.; Canary, J. W. *Inorg. Chim. Acta* **1995**, *239*, 29.

(8) Brownstein, S. K.; Plouffe, P. Y.; Bensimon, C.; Tse, J. *Inorg. Chem.* **1994**, *33*, 354.

(9) Mandel, J. B.; Maricondi, C.; Douglas, B. E. *Inorg. Chem.* **1988**, *27*, 2990.

(10) Goodson, P. A.; Oki, A. R.; Glerup, J.; Hodgson, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 6248.

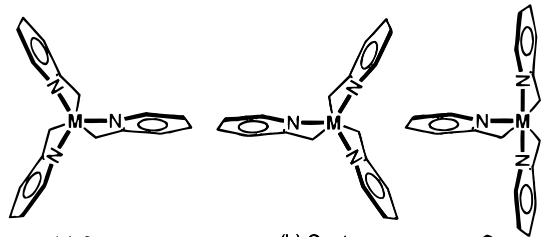
(11) Murthy, N. N.; Karlin, K. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1236.

(12) Wei, N.; Lee, D.-H.; Murthy, N. N.; Tyeklár, Z.; Karlin, K. D.; Kaderli, S.; Jung, B.; Zuberbühler, A. D. *Inorg. Chem.* **1994**, *33*, 4625.

(13) Zang, Y.; Dong, Y.; Que, L., Jr.; Kauffmann, K.; Münck, E. *J. Am. Chem. Soc.* **1995**, *117*, 1169.

(14) Harata, M.; Jitsukawa, K.; Masuda, H.; Ensaga, H. *J. Am. Chem. Soc.* **1994**, *116*, 10817.

10.1021/ic9803098 CCC: $15.00



(a) C_3, Δ (b) C_3, Λ C_σ

Figure 1. $[M(TPA)]^{n+}$ C_3 and C_σ conformations. View is down the metal-tertiary amine axis.

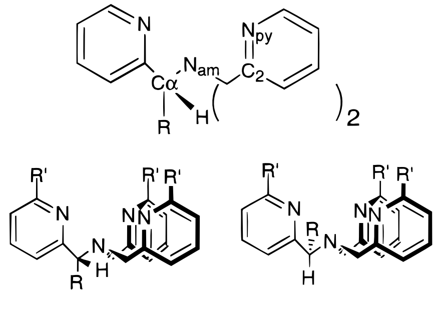


Figure 2. Conformations and numbering scheme.

propeller. The two possible propeller-like stereoisomers (Figure 1a,b) are conformational enantiomers.

The scarcity of chiral, C_3 symmetric ligands[15] led to the proposal of modifying TPA by attaching substituents in appropriate positions to influence the overall structure of the corresponding coordination complexes. Our strategy for the control of the propeller-like twist derives from the incorporation of one chiral center on one arm of the tripodal ligand. Examination of CPK (Corey−Pauling−Koltun) molecular models of trigonal bipyramidal $[M(TPA)X]^+$ complexes indicated that an alkyl or aryl substituent on one arm ("R" in Figure 2) should influence the ligand in the coordination complex to adopt a particular helical asymmetry dictated by the absolute configuration of the substituent-bearing carbon atom (Figure 2). Two binding conformations are possible, the "anti" conformation in which the α-substituent points away from the pyridyl groups, and the "syn" conformation in which the α-substituent points toward one pyridyl group. The syn conformation should be less stable due to the presence of a *syn*-pentane type interaction between the α-substituent and one of the pyridyl groups.[16] The α-substituted TPA complexes would demonstrate pseudo C_3 symmetry with an asymmetric environment surrounding the fifth coordination site in a $[M^{II}(\alpha\text{-R-TPA})X]^{n+}$ moiety. Subsequent synthesis of other chiral TPA derivatives, containing substituents attached to the 6-positions of the pyridyl rings ("R′" in Figure 2) or mixed tripodal ligands with pyridine and other heterocyclic pendants should form pseudo C_3 symmetric coordination complexes with more highly asymmetric environments encompassing the available electrophilic apical site.

The initial set of ligands selected for this study were *N*,*N*-bis[(2-pyridyl)methyl]-1-(2-pyridyl)ethanamine (**1**, α-MeTPA), *N*,*N*-bis[(6-phenyl-2-pyridyl)methyl]-1-(2-pyridyl)ethanamine (**2**, α-$MePh_2TPA$), *N*,*N*-bis[(2-quinolyl)methyl]-1-(2-pyridyl)ethanamine (**3**, α-MeBQPA), and *N*,*N*-bis[(2-pyridyl)methyl](phenyl)(2-pyridyl)methanamine (**4**, α-PhTPA). TPA derivatives **1** and **4** differ in the size of the R substituent. Ligands **2** and **3** present greater steric hindrance on the heterocycle arms, which was observed previously to increase the degree of twist observed in crystallographic structures of Cu(I) and Cu(II) complexes.[17−20] Semiempirical (MNDO) calculations[21] of $[Zn(\alpha\text{-MeTPA})Cl]^+$, $[Zn(\alpha\text{-PhTPA})Cl]^+$, and $[Zn(\alpha\text{-MeBQPA})Cl]^+$ cations supported the predictions from examination of molecular models that the anti conformation would be more stable than the syn isomer by 1.5−2.5 kcal/mol, and that the complex with a carbon center configuration of *R* would display a Λ (left-handed) propeller-like twist.

Inspection of the literature revealed that a few examples of tripodal ligands with chiral arms had been reported.[8,22−26] Our objectives in the present study was to conduct a detailed analysis of the conformational behavior of the ligands in the complexes, including the factors that dictate the axial chirality of the complexes.

Experimental Section

Syntheses. $[Cd(\alpha\text{-MeTPA})I_2]$. A solution of CdI_2 (58.0 mg, 0.158 mmol) in 0.5 mL of methanol was added dropwise via pipet to a hot solution of **1**[1] (α-MeTPA, 48.2 mg, 0.158 mmol) in 0.5 mL of methanol. A white precipitate formed immediately and was collected and dried in vacuo to yield 92.0 mg (86.6%). ^1H NMR (300 MHz, DMSO-d_6): δ 8.70 (d, $J = 4.4$ Hz, 1H), 8.62 (d, $J = 3.9$ Hz, 1H), 8.43 (d, $J = 4.3$ Hz, 1H), 8.05−8.00 (m, 1H), 7.89−7.84 (m, 1H), 7.67−7.38 (m, 5H), 7.26−7.22 (m, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 4.71 (q, $J = 6.6$ Hz, 1H), 4.48 (d, $J_{gem} = 15.0$ Hz, 1H), 4.36 (d, $J_{gem} = 15.0$ Hz, 1H), 3.86 (d, $J_{gem} = 16.5$ Hz, 1H), 3.80 (d, $J_{gem} = 16.5$ Hz, 1H), 1.76 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.5, 154.7, 154.1, 147.8, 147.7, 147.3, 140.2, 139.6, 138.8, 125.0, 124.1, 123.9, 123.5, 123.2, 61.5, 59.1, 53.5, 10.9. Anal. Calcd for $C_{19}H_{20}N_4CdI_2$: C, 34.03; H, 3.01; N, 8.35. Found (R form): C, 34.16; H, 2.81; N, 8.19. Found (S form): C, 33.81; H, 3.08; N, 8.32.

$[Zn(\alpha\text{-MeTPA})Cl]ClO_4$. (**Caution!** *Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantity and with caution.*)[27] A solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (60.5 mg, 0.163 mmol) in 0.4 mL of methanol was added via pipet to a solution of α-MeTPA[1] (49.5 mg, 0.163 mmol) in 0.4 mL of methanol. After stirring for about 10 min, a solution of NaCl (9.53 mg, 0.163 mmol) in 0.4 mL H_2O was added. The mixture was left in refrigerator for several h during which time a white precipitate formed. The precipitate was collected and dried (33.4 mg, 40.6%). ^1H NMR (300 MHz, CD_3COCD_3): δ 9.19−9.10 (m, 3H), 8.33−8.20 (m, 3H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.84−7.76 (m, 5H), 4.83 (d, $J_{gem} = 16.7$ Hz, 1H), 4.53 (d, $J_{gem} = 16.4$ Hz, 1H), 4.38 (q, $J = 6.8$ Hz, 1H), 4.21 (d, $J_{gem} = 16.7$ Hz, 1H), 4.17 (d, $J_{gem} = 16.4$ Hz, 1H), 1.94 (d, $J = 6.8$ Hz, 3H). Anal. Calcd for $C_{19}H_{20}N_4ZnCl_2O_4 \cdot 2H_2O$: C, 42.21; H, 4.47; N, 10.36. Found (R form): C, 42.39; H, 4.12; N, 10.43. Found (S form): C, 42.40; H, 3.98; N, 10.40.

The racemic precipitate was recrystallized from acetone/ether/toluene to obtain X-ray quality crystals. Anal. Calcd for $[Zn(MeTPA)Cl]ClO_4 \cdot 0.5C_7H_8 \cdot 0.5H_2O$: C, 48.28; H, 4.50; N, 10.01. Found: C, 48.46; H, 4.39; N, 10.13.

---

(15) Moberg, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 248.

(16) Wang, X.; Erickson, S. D.; Iimori, T.; Still, W. C. *J. Am. Chem. Soc.* **1992**, *114*, 4128.

(17) Wei, N.; Murthy, N. N.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 6093.

(18) Wei, N.; Murthy, N. N.; Chen, Q.; Zubieta, J.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 1953.

(19) Chuang, C.-L.; Lim, K.; Chen, Q.; Zubieta, J.; Canary, J. W. *Inorg. Chem.* **1995**, *34*, 2562.

(20) Chuang, C.-L.; Lim, K.; Canary, J. W. *Supramol. Chem.* **1995**, *5*, 39.

(21) *Spartan 3.01*; Wavefunction, Inc.: 18401 Von Karman Ave., Suite 370, Irvine, CA.

(22) Ohtani, Y.; Utsuno, S. *Chem. Lett.* **1980**, 465.

(23) Endo, I.; Horikoshi, S.; Utsuno, S. *Chem. Commun.* **1981**, 296.

(24) Utsuno, S.; Miyamae, H.; Horikoshi, S.; Endo, I. *Inorg. Chem.* **1985**, *24*, 1348.

(25) Sakurai, T.; Oi, H.; Nakahara, A. *Inorg. Chim. Acta* **1984**, *92*, 131.

(26) Hojland, F.; Toftlund, H.; Yde-Andersen, S. *Acta Chem. Scand. A* **1983**, *37*, 251.

(27) *Chem. Eng. News* **1983**, *61*, 4.

[Cu(α-MeTPA)Cl]ClO$_4$. A solution of Cu(ClO$_4$)$_2$·H$_2$O (73.8 mg, 0.200 mmol) in 0.4 mL of methanol was added via pipet to a solution of α-MeTPA[1] (60.7 mg, 0.200 mmol) in 0.4 mL of methanol. After stirring for about 10 min, a solution of NaCl (11.7 mg, 0.200 mmol) in 0.4 mL of water was added. Greenish crystals formed after cooling the mixture in an ice bath for ca. 20 min. The crystals were collected and dried (65.0 mg, 64.6%). Anal. Calcd for $C_{19}H_{20}N_4CuCl_2O_4$: C, 45.38; H, 4.01; N, 11.14. Found (R form): C, 45.13; H, 4.26; N, 10.93. Found (S form): C, 45.19; H, 3.99; N, 10.9.

6-Bromo-2-pyridylmethyl Bromide, 8. The compound 6-bromo-2-pyridinemethanol (**7**, 21.8 g, 0.116 mol) was added to 300 mL of 48% HBr. The solution was heated to 120 °C for 4 h. After cooling, the solution was made basic with sodium bicarbonate until pH = 5−6, extracted with ether, and dried over Na$_2$SO$_4$. Evaporation of the solvent gave 24.8 g of **8** (85%). ^{1}H NMR (200 MHz, CDCl$_3$): 7.60−7.39 (m, 3H), 4.50 (s, 2H).

***N,N*-Bis[(6-bromo-2-pyridyl)methyl]-1-(2-pyridyl)ethanamine, 10.** Diisopropylethylamine (2.96 g, 22.9 mmol) and **8** (2.88 g, 11.5 mmol) were added to 50 mL of THF.[18] To this solution was added dropwise 1-(2-pyridyl)ethylamine[1] (**9**, 0.70 g, 5.73 mmol). The mixture was stirred at ambient temperature for 3 days, during which a white precipitate formed. After the solution was filtered, the filtrate was concentrated in vacuo to give a brown oil which was purified by column chromatography on silica gel with CH$_2$Cl$_2$/ether (3:1, R_f = 0.43) to give pure product **10** (2.11 g, 74%). ^{1}H NMR (200 MHz, CDCl$_3$): 8.52−8.48 (m, 1H), 7.65−7.07 (m, 9H), 4.02 (q, J = 6.9 Hz, 1H), 3.92 (d, J_{gem} = 15.5 Hz, 2H), 3.72 (d, J_{gem} = 15.5 Hz, 2H), 1.48 (d, J = 6.9 Hz, 3H). ^{13}C NMR (50 MHz, CDCl$_3$): 162.6, 149.4, 141.6, 139.1, 136.6, 127.5, 126.5, 123.2, 122.5, 121.8, 61.3, 56.9, 15.6. MS (ESI): 485 (100, M + Na$^+$), 463 (4, M + H$^+$).

***N,N*-Bis[(6-phenyl-2-pyridyl)methyl]-1-(2-pyridyl)ethanamine, 2 (α-MePh$_2$TPA).** To a stirred solution of **10** (0.46 g, 1.0 mmol) and Pd(PPh$_3$)$_4$ (0.069 g, 0.06 mmol) in 4 mL of dry toluene under nitrogen was added 2 mL of 2 M Na$_2$CO$_3$ and phenyl boronic acid (0.29 g, 2.4 mmol) in 1 mL of methanol. The vigorously stirred mixture was heated to reflux for 8 h. It was then allowed to cool and was partitioned between 100 mL of CHCl$_3$ and 10 mL of 2 M Na$_2$CO$_3$ containing 1 mL of concentrated NH$_3$. The organic layer was dried (Na$_2$SO$_4$) and concentrated under reduced pressure. Flash chromatography on basic alumina (CH$_2$Cl$_2$/EtOAc 20:1, R_f = 0.32) gave **2** (0.34 g, 84.0%). The product was further purified by recrystallization from methanol. ^{1}H NMR (200 MHz, CDCl$_3$): 8.60−8.57 (m, 1H), 8.03−7.98 (m, 4H), 7.72−7.36 (m, 14H), 7.14−7.08 (m, 1H), 4.23 (q, J = 6.8 Hz, 1H), 4.15 (d, J_{gem} = 15.0 Hz, 2H), 3.96 (d, J_{gem} = 15.0 Hz, 2H), 1.65 (d, J = 6.8 Hz, 3H). ^{13}C NMR (50.3 MHz, CDCl$_3$): 163.2, 161.0, 156.9, 149.3, 140.0, 137.4, 136.5, 129.2, 129.1, 127.4, 123.4, 122.3, 121.6, 118.9, 61.1, 57.5, 15.4. MS (ES) *m*/*e*: 495 (45, M + K$^+$), 479 (100, M + Na$^+$), 457 (57, M + H$^+$). Anal. Calcd for $C_{31}H_{28}N_4$: C, 81.55; H, 6.18; N, 12.27. Found (R form): C, 81.63; H, 6.33; N, 12.41. Found (S form): C, 81.76; H, 6.18; N, 12.51.

[Cd(α-MePh$_2$TPA)I$_2$]. A solution of CdI$_2$ (80.6 mg, 0.220 mmol) in 0.5 mL of MeCN was added dropwise via pipet to a hot solution of **2** (100.6 mg, 0.220 mmol) in 3.3 mL of MeCN. A white precipitate formed after sitting overnight at 5 °C. The precipitate was collected and washed with 2 mL of MeCN. The sample was dried in vacuo to yield 123.5 mg (68.2%) of a white powder. Anal. Calcd for $C_{31}H_{28}N_4CdI_2$: C, 45.25; H, 3.43; N, 6.81. Found (R form): C, 45.03; H, 3.20; N, 6.94. Found (S form): C, 45.12; H, 3.22; N, 6.74.

[Zn(α-MePh$_2$TPA)Cl]ClO$_4$. A solution of Zn(ClO$_4$)$_2$·6H$_2$O (58.1 mg, 0.156 mmol) in 0.4 mL of H$_2$O was added to a hot solution of **2** (71.3 mg, 0.156 mmol) in 3 mL of MeCN. While maintaining the temperature a solution of NaCl (11.0 mg, 0.188 mmol) in 0.4 mL of H$_2$O was added. The solvent was partially evaporated at ambient temperature and the clear solution was allowed to stand overnight. White crystals formed which were collected and dried in vacuo. The yield was 80.7 mg (78.7%). Anal. Calcd for $C_{31}H_{28}N_4ZnCl_2O_4$: C, 56.68; H, 4.30; N, 8.53. Found (R form): C, 56.90; H, 4.62; N, 8.80. Found (S form): C, 56.94; H, 4.44; N, 8.77.

Phenyl-2-pyridylmethanamine, 6. 2-Benzoylpyridine (18.5 g, 0.101 mol) and hydroxylamine hydrochloride (13.5 g, 0.194 mol) were dissolved in 90 mL of pyridine. The mixture was heated to reflux for 4 h. The reaction mixture was cooled and chilled water was added, resulting in a white precipitate. The precipitate was isolated by filtration and dried (16.5 g, 82.4%). The crude product was used directly in the next step without further purification.[28]

The ketoxime (14.0 g, 0.0706 mol) was dissolved in 150 mL of 95% EtOH with heating. After cooling to ambient temperature, 75 g of zinc dust and 75 mL of acetic acid were added over 3 h. The reaction mixture was stirred overnight. After filtration, the filtrate was concentrated in vacuo. Water was added and evaporated several times to remove acetic acid. The mixture was basified with strong KOH solution and extracted with ether. The organic layer was dried over Na$_2$SO$_4$. After removal of the solvent, the crude product was distilled using a Kügelrohr apparatus, affording the colorless product **6** (10.7 g 82.3%). ^{1}H NMR (300 MHz, CDCl$_3$): 8.58 (d, J = 4.5 Hz, 1H), 7.63−7.12 (m, 8H), 5.26 (s, 1H), 2.35 (br s, 2H).

***N,N*-Bis(2-pyridylmethyl)-phenyl-2-pyridylmethanamine (α-Ph-TPA), 4.** Picolyl chloride hydrochloride (3.86 g, 23.6 mmol) was dissolved in 6 mL of water. Amine **6** (2.17 g, 11.8 mmol) was then added. The mixture was then warmed to 70 °C, and 4.6 mL of a 10M NaOH solution was added slowly. Stirring was continued at this temperature for another 4 h. After cooling, the reaction mixture was extracted with CHCl$_3$ and the organic layers were dried over Na$_2$SO$_4$. The solvent was removed in vacuo and the crude product was chromatographed on basic alumina (CH$_2$Cl$_2$/EtOAc = 4:1, R_f = 0.40). The yield of pure **4** was 1.21 g (28.0%). ^{1}H NMR (300 Hz, CDCl$_3$): 8.59 (d, J = 4.6 Hz, 1H), 8.49 (d, J = 4.7 Hz, 2H), 7.67−7.07 (m, 14H), 5.20 (s, 1H), 3.93 (s, 4H). MS (ESI) *m*/*e*: 367 (100), 368 (30), 369 (3).

[Zn(α-PhTPA)Cl]ClO$_4$. Compound **4** (523.5 mg, 1.43 mmol) was dissolved in 0.5 mL of methanol. Zn(ClO$_4$)$_2$·6H$_2$O (531.4 mg, 1.43 mmol) in 0.8 mL of methanol was added. After stirring for a while NaCl (83.4 mg, 1.43 mmol) in 0.5 mL of H$_2$O was added slowly, resulting in immediate precipitation. The precipitate was collected and dried (0.771 g, 67.7%). Recrystallization from 50% methanol/H$_2$O gave X-ray-quality crystals. ^{1}H NMR (300 MHz, CD$_3$CN): 9.17 (d, J = 5.2 Hz, 1H), 9.30 (d, J = 5.2 Hz, 1H), 8.98 (d, J = 5.0 Hz, 1H), 8.12−6.84 (m, 14H), 5.28 (s, 1H), 4.22 (d, J_{gem} = 16.1 Hz, 1H), 4.13 (d, J_{gem} = 16.5 Hz, 1H), 4.00 (d, J_{gem} = 16.5 Hz, 1H), 3.77 (d, J_{gem} = 16.1 Hz, 1H). Anal. Calcd for $ZnC_{24}H_{22}N_4Cl_2O_4$: C, 50.86; H, 3.91; N, 9.89. Found: C, 50.67; H, 3.72; N, 9.83.

X-ray Structures. Intensity data for [Zn(α-MeTPA)Cl](ClO$_4$) and [Zn(α-PhTPA)Cl](ClO$_4$) were collected at −80 °C (to minimize crystal decay) on a Rigaku AFC6R diffractometer equipped with a 12 kW rotating anode generator, a graphite monochromator (Cu Kα, λ = 1.541 78 Å) and a low-temperature apparatus which funneled a chilled stream of nitrogen gas onto the mounted crystal. Structures were solved by a combination of Patterson methods, PHASE,[29] and direct methods, DIRDIF,[30] using the TEXSAN software package.[31] Crystallographic data are listed in Table 1. Details on the structure of [Zn(α-MeBQPA)Cl](ClO$_4$) were included in the preliminary report.[1]

Spectra. Solutions in methanol of the ligands and complexes were prepared for the CD and the UV−vis studies. For CD spectra (1 mm cell) the concentrations used were (0.8−2.2) × 10^{-4} M for the series of solutions with α-MeBQPA as the ligand, (0.6−1.6) × 10^{-4} M for α-MePh$_2$TPA, and (0.9−2.3) × 10^{-4} M for α-MeTPA. For the UV−vis studies (10 mm cell) the concentrations used were (6.6−7.7) × 10^{-6} M for α-MeBQPA, (6.4−7.4) × 10^{-6} M for α-MePh$_2$TPA, and (7.2−10.5) × 10^{-6} M for α-MeTPA. Variable temperature ^{1}H NMR experiments were conducted on a 300 MHz Varian Gemini instrument. Concentrations were 6−10 mg/0.75 mL of sovent. Frozen EPR spectra of [Cu(α-MeTPA)Cl]ClO$_4$ and [Cu(α-BQPA)Cl]ClO$_4$ were determined in glassy ethanol/methanol (1:9) and glassy DMF/CHCl$_3$ (1:1) solutions, respectively, at −196 °C utilizing a Varian E-4 spectrometer. The

---

(28) Niemers, E.; Hiltmann, R. *Synthesis* **1976**, 593.

(29) Calabrese, J. C. Ph.D. Dissertation Thesis, University of Wisconsin—Madison, 1972.

(30) Beurskens, P. T. In *Technical Report 1984/1*; Crystallography Laboratory: Toernooiveld 1, 6525 ED Nijmegen, University of Nijmegen, The Netherlands, 1984.

(31) *Single-Crystal Structure Analysis Software*, Version 5.0; Molecular Structure Corporation: The Woodlands, TX, 1985.

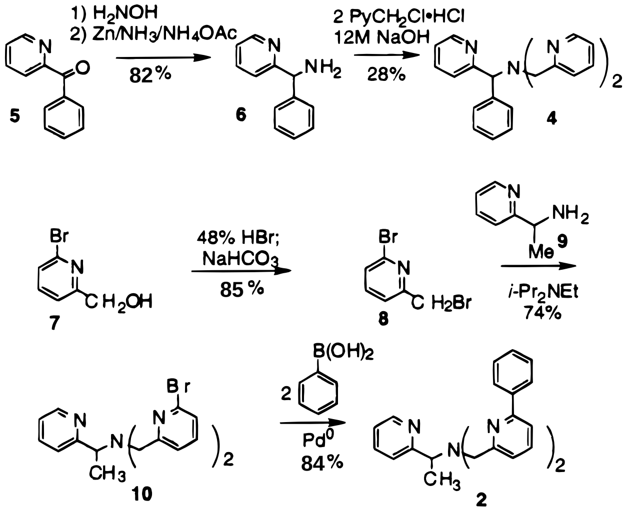


Figure 3. Synthesis of ligands.

Table 1. Synopsis of Structural Parameters Derived from X-ray Crystallographic Data for Racemic [Zn(α-MeTPA)Cl]$ClO_4\cdot 0.5C_7H_8$ and [Zn(α-PhTPA)Cl]ClO_4

	[Zn(α-MeTPA)Cl]-$ClO_4\cdot 0.5C_7H_8$	[Zn(α-PhTPA)Cl]-ClO_4
empirical formula	$C_{22.5}H_{20}Cl_2N_4O_4Zn$	$C_{24}H_{22}Cl_2N_4O_4Zn$
fw	546.72	566.75
temp (°C)	−80	−80
cryst color, habit	colorless, block	colorless, block
cryst dimens (mm)	0.450 × 0.075 × 0.100	0.200 × 0.100 × 0.100
cryst system	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*P*2_1/*c* (No. 14)
Z value	8	4
lattice params	$a = 26.630(5)$ Å	$a = 8.419(9)$ Å
$b = 14.022(2)$ Å	$b = 13.12\ (1)$ Å	
$c = 13.331(3)$ Å	$c = 21.47\ (2)$ Å	
$\beta = 101.35(2)°$	$\beta = 97.93\ (7)°$	
$V = 4881(2)$ Å^3	$V = 2349\ (4)$ Å^3	
D_{calcd} (g/cm^3)	1.488	1.602
F_{000}	2232	1160
$\mu_{CuK\alpha}$ (cm^{-1})	37.80	39.48
no. of observns ($I > 3.00\sigma(I)$)	2791	2307
no. of variables	366	334
reflcn/param ratio	7.63	6.91
residuals: *R*; R_w	0.066; 0.086	0.055; 0.064
goodness-of-fit indicator	3.37	1.96
max/min peaks in final diff. map (e$^-$/Å^3)	0.94; −0.58	0.44; −0.40

concentration of the solutions were 0.0015 and 0.0010 M, respectively. The microwave frequency was 9.22 × 10^9 Hz at 2 mW power, while the modulation was 4.0 G at 100 kHz. The spectra were referenced to external diphenylpicrylhydrazyl radical (DPPH).

Results

Synthesis. In general, the ligands reported in this paper were prepared from the alkylation of primary amines with halomethylpyridines. Racemic samples were synthesized and utilized for coordination chemistry studies including the preparation of samples for crystallographic analysis. Materials for circular dichroism studies were obtained subsequently from enantiomerically pure primary amines.

The syntheses of α-MeTPA[26] and α-MeBQPA were described in the previous report.[1] The ligand α-PhTPA was prepared from phenylpyridyl ketone **5** by formation of the oxime, reduction, and alkylation with picolyl chloride. The synthesis of compound **2** (α-MePh$_2$TPA, Figure 3) began with 6-bromo-2-pyridinemethanol **7**.[32] Treatment with aqueous HBr followed by mild base provided compound **8**. Reaction of 1-(2-pyridyl)ethylamine **9** with **8** in DMF in the presence of diisopropylethylamine (DIPEA) gave the dibromotripod **10**. Suzuki coupling[33,34] with phenylboronic acid provided the target ligand **2** in good yield (91%).

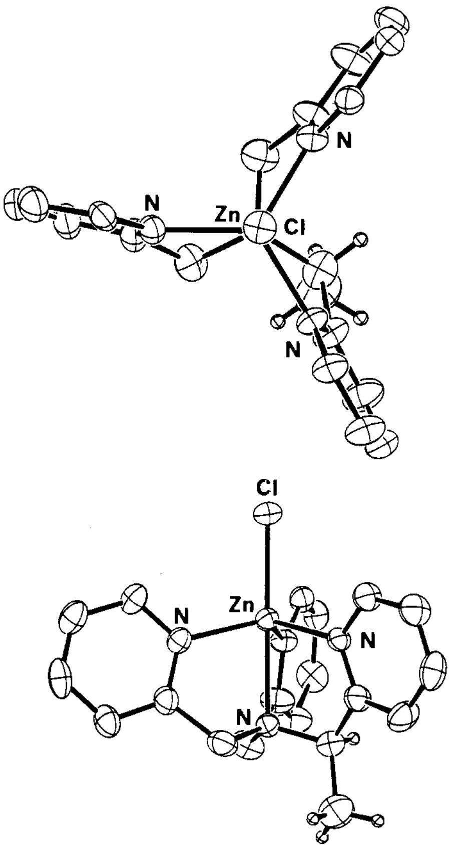


Figure 4. X-ray crystallographic structure of [Zn(α-MeTPA)Cl](ClO_4). Some hydrogens omitted for clarity.

In general, coordination complexes were prepared simply by mixing homogeneous solutions of ligand and metal salts under conditions suitable for crystallization of the complexes. In most cases, the solids were found to display correct elemental analysis without further purification.

X-ray Structures. X-ray crystallographic studies were undertaken on the racemic coordination complexes [Zn(α-MeTPA)Cl]ClO_4, [Zn(α-MeBQPA)Cl]ClO_4,[1] and [Zn(α-PhTPA)Cl]ClO_4 to determine the nuclearity, tripodal ligand conformation and metal coordination geometry.

Colorless, block-shaped crystals of a zinc(II) complex of α-MeTPA were obtained by recrystallization from a toluene/diethyl ether/acetone solvent system. The structure, solved in the monoclinic space group *C*2/*c*, was formulated as [Zn(α-MeTPA)Cl]$ClO_4\cdot 0.5C_7H_8$. The perchlorate anion is disordered in the structure and was partially modeled by two orientations employing four pairs of oxygens around a central chlorine atom. Highly disordered solvate molecules are present in the structure, including a modeled toluene molecule (half-equivalent). ORTEP representations of [Zn(α-MeTPA)Cl]$^+$ cation are shown in Figure 4. The [Zn(α-MeTPA)Cl]$^+$ is structurally similar to [Zn(TPA)Cl]$^+$ [7] as a pentacoordinate zinc(II) cation resides in

---

(32) Cai, D.; Hughes, D. L.; Verhoeven, T. R. *Tetrahedron Lett.* **1996**, *37*, 2537.

(33) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(34) Aliprantis, A. O.; Canary, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 6985.

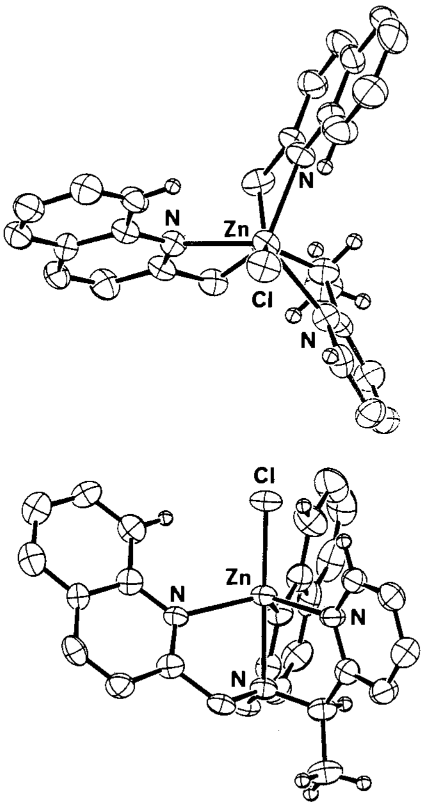


Figure 5. X-ray crystallographic structure of [Zn(α-MeBQPA)-Cl](ClO$_4$). Some hydrogens omitted for clarity.

a distorted trigonal bipyramidal environment with the pyridyl nitrogens coordinated in the equatorial positions and the tertiary amine nitrogen in an axial position. The zinc(II) cation is perched 0.46 Å above the least-squares plane defined by the pyridyl nitrogens. Intramolecular Zn$-$N$_{py}$ bond distances range from 2.05 to 2.09 Å and chelate angles (N$_{am}-$Zn$-$N$_{py}$) from 76 to 78° which are similar to the values in other trigonal bipyramidal zinc/TPA complexes.[7,11] The Zn$-$N$_{am}$ bond (2.28 Å) is longer than the Zn$-$N$_{py}$ bonds. The chlorine resides in an apical site, nearly on the Zn$-$N$_{am}$ axis as indicated by the N$_{am}-$Zn$-$Cl angle of 178.0(1)°. The conformation of the ligand in the complex is anti. The three pyridine rings are tilted in the same direction, with angles between the planes containing the pyridine rings and the Zn$-$N$_{am}$ axis of 7.6, 7.0, and 10.2°. The representation shown in Figure 4 shows that for a C_α configuration of *R*, a Λ propeller-like twist of the pyridine rings is adopted.

The structure of racemic [Zn(α-MeBQPA)Cl]ClO$_4$ was solved in the monoclinic space group *C*2/*c* with the asymmetric unit consisting of a [Zn(α-MeBQPA)Cl]$^+$ cation and a noncoordinating perchlorate anion.[1] The perchlorate anion was not disordered in this structure. ORTEP diagrams of a [Zn(α-MeBQPA)Cl]$^+$ cation are shown in Figure 5. The figure reveals a pentacoordinate zinc(II) in a distorted trigonal bipyramidal environment with the heterocyclic nitrogens coordinated in the equatorial positions and the tertiary amine nitrogen in an axial site. Chloride resides in the available apical site but is not on the Zn$-$N$_{am}$ axis as the bond angle N$_{am}-$Zn$-$Cl is 166.2(2)°. Steric hindrance between the chloride and the quinoline 8-hydrogens is evident as the chloride is forced to tilt away. Steric hindrance influences the tilt of the heterocyclic rings relative to the Zn$-$N$_{am}$ axis. The zinc(II) cation is perched 0.48 angstrom above the least-squares plane defined by the pyridyl nitrogens. Intramolecular Zn$-$N$_{quin}$ bond distances are in the relatively narrow range of 2.14$-$2.16 Å, and the Zn$-$N$_{am}$ bond length is 2.20 Å. The average tilt angle of the pyridine planes with the N$_{am}-$Zn axis is 15.9° with values 10.3, 23.1, and 14.2°. The resulting twist is in the same direction relative to C_α as observed in the α-MeTPA complex.

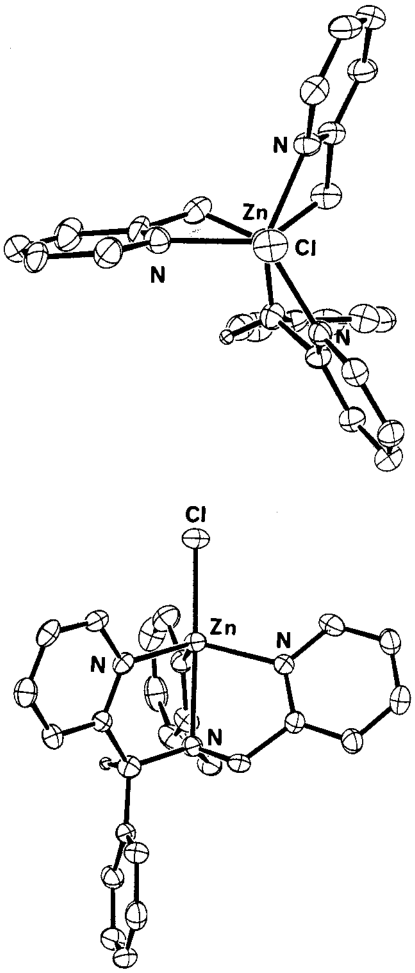


Figure 6. X-ray crystallographic structure of [Zn(α-PhTPA)Cl](ClO$_4$). Some hydrogens omitted for clarity.

The structure of racemic [Zn(α-PhTPA)Cl]ClO$_4$ (Figure 6) was solved in the monoclinic space group *P*2$_1$/*c* with the asymmetric unit consisting of a [Zn(α-PhTPA)Cl]$^+$ cation and a disordered perchlorate anion which was partially modeled by six oxygens emanating from a central chlorine atom. Intramolecular Zn$-$N$_{py}$ bond distances range from 2.05 to 2.10 Å and the Zn$-$N$_{am}$ bond is 2.28 Å. The tilt of the pyridine planes with respect to the N$_{am}-$Zn axis is 11.4, 15.3, and 10.1°, forming a propeller twist with the same directional sense relative to C_α as observed in the other two structures.

Spectra. The spectroscopic properties of the enantiomerically pure ligands and their complexes with Zn(II), Cu(II), and Cd(II) ions were studied by UV$-$vis and circular dichroism spectroscopy. The spectra of the ligands and their complexes appear in Figures 7$-$9, and some extinction coefficients are listed in Table 2. The UV$-$vis spectra of α-MeTPA and its complexes in methanol show that the $\pi-\pi^*$ transitions in the ligand are affected only slightly when the ligand is complexed with Cu(II) or Cd(II) which causes a hypsochromic shift of 2 nm; a hyperchromic effect can also be observed. The maxima around 260$-$262 nm for the ligand and complexes correspond to the pyridine B band. The n$-\pi^*$ is not observed as expected due

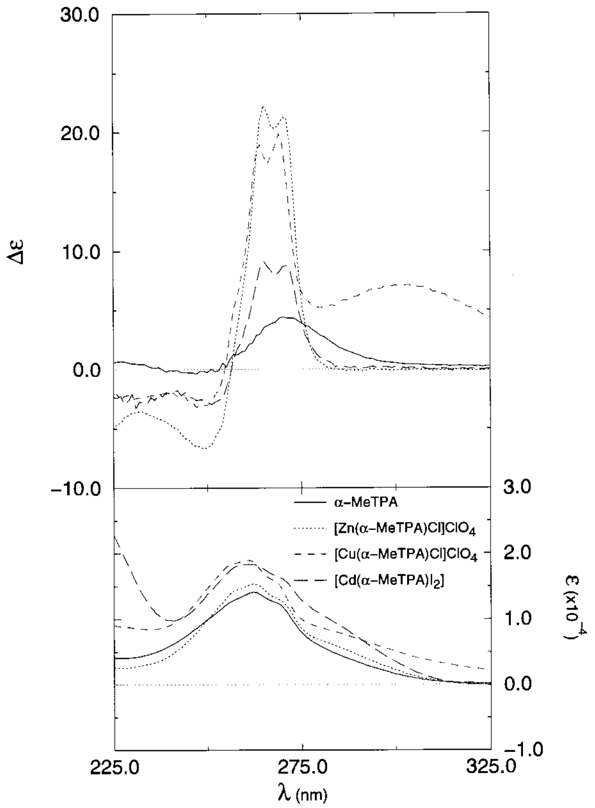


Figure 7. Circular dichroism and UV−vis spectra (×10^{-4}) (methanol) for *S*-α-MeTPA, [Cd(*S*-α-MeTPA)I$_2$], [Zn(*S*-α-MeTPA)Cl]ClO$_4$, and [Cu(*S*-α-MeTPA)Cl]ClO$_4$.

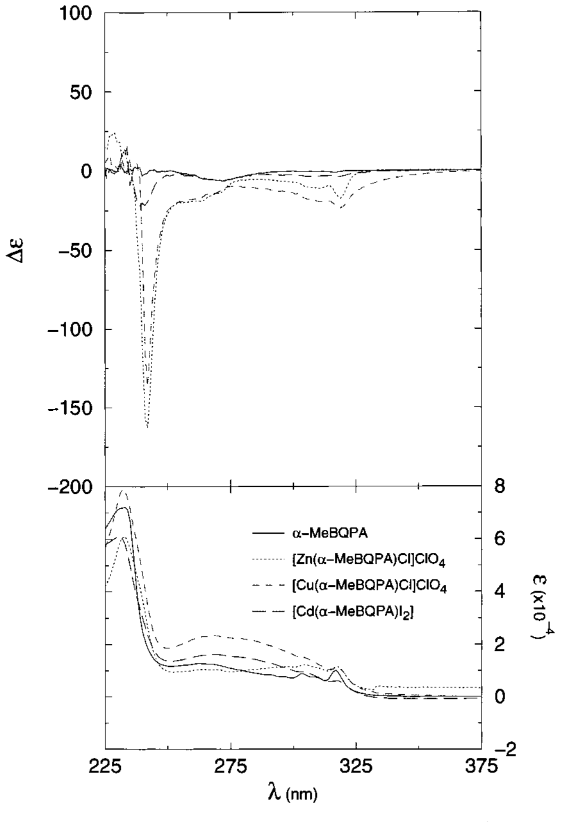


Figure 8. Circular dichroism and UV−vis spectra (×10^{-4}) (methanol) for *S*-α-MeBQPA, [Cd(*S*-α-MeBQPA)I$_2$], [Zn(*S*-α-MeBQPA)Cl]ClO$_4$, and [Cu(*S*-α-MeBQPA)Cl]ClO$_4$.

to the strong B band. The spectra of α-MePh$_2$TPA and its complexes in methanol show the typical $\pi-\pi^*$ transition (B-band) of the pyridine (278 and 282 nm) and benzene (250 nm) chromophores. The latter is clearly distinguishable in the free ligand and the Zn(II) complex; in the Cd(II) complexes the transition due to the benzene appears as a shoulder. In this case a hypochromic effect is seen when the ligand complexes Zn(II) or Cd(II), and the Zn(II) complex shows also a bathochromic shift in the pyridine B band absorption.

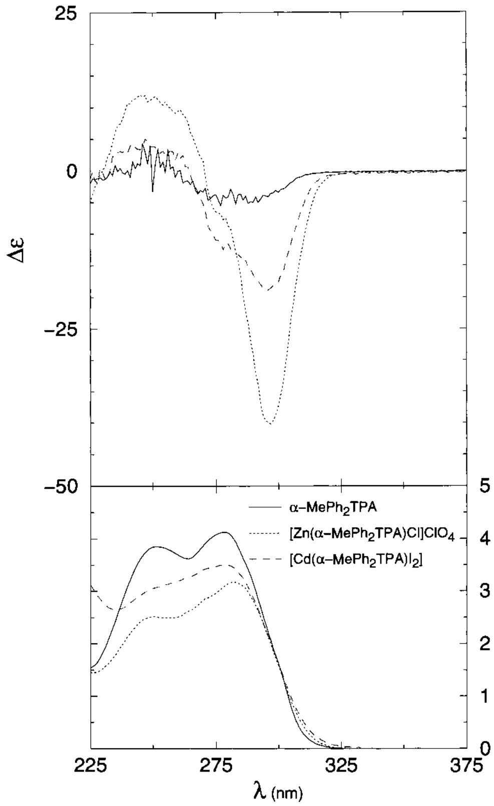


Figure 9. Circular dichroism and UV−vis spectra (×10^{-4}) (methanol) for *S*-α-MeBPPA, [Cd(*S*-α-MeBPPA)I$_2$], and [Zn(*S*-α-MeBPPA)Cl]-ClO$_4$.

Table 2. Isotropic and Anisotropic Extinction Coefficients and Dissymmetry Factors (*g*) of Free Ligands and Metal−Ligand Complexes of *(S)*-α-MeTPA (265 nm), *(S)*-α-MePh$_2$TPA (307 nm), and *(S)*-α-MeBQPA (243 nm)

	$\Delta\epsilon$	ϵ (×10^{-4})	*g* (×10^3)
α-MeTPA	3.55	1.33	0.27
[Zn(α-MeTPA)Cl]ClO$_4$	22.29	1.45	1.54
[Cu(α-MeTPA)Cl]ClO$_4$	17.98	1.68	1.07
[Cd(α-MeTPA)I$_2$]	9.11	1.75	0.52
α-MePh$_2$TPA	−0.86	0.52	0.16
[Zn(α-MePh$_2$TPA)Cl]ClO$_4$	−17.59	0.68	2.60
[Cd(α-MePh$_2$TPA)I$_2$]	−8.09	0.76	1.06
α-MeBQPA	0.34	1.66	0.02
[Zn(α-MeBQPA)Cl]ClO$_4$	−139.23	2.19	6.34
[Cu(α-MeBQPA)Cl]ClO$_4$	−111.54	2.97	3.75
[Cd(α-MeBQPA)I$_2$]	−16.92	2.09	0.81

The UV−vis spectra of α-MeBQPA and its metal complexes show the strong E$_1$ band of the quinoline rings (232 nm), the B-band of the pyridine (263, 270 nm), and the B band of the quinoline (303, 317 nm). As with α-MePh$_2$TPA there is a small hypochromic effect when the ligand is complexed with Zn(II) or Cd(II), and a hyperchromic effect with Cu(II). The Cu(II) and Cd(II) complexes show a bathochromic shift in the pyridine B band, compared to the free ligand (from 263 to 270 nm). The complex with Zn(II) does not show a distinguishable absorption in this region. The B band from the quinoline is clearly present in the free ligand and the Cu(II) and Zn(II) complexes, but not in the Cd(II) complex.

In general the UV−vis data present all the electronic features that are expected from these aromatic, tripodal tetradentate ligands and complexes. There are small shifts and changes in intensity upon complexation, which are dependent on the nature of the metal ion. As expected, the metal ion coordination geometry has little effect on the isotropic transitions.

The CD spectra of the ligands and their complexes in methanol (Figures 7−9) show significant enhancement of the signal when the Zn(II) and Cu(II) complexes are compared with the free ligand or the Cd(II) complexes. In the case of [Zn(α-MeBQPA)Cl](ClO_4) and [Cu(α-MeBQPA)Cl](ClO_4), the CD spectra show Cotton effects centered approximately at the wavelength of maximum absorption in the UV−vis spectra (232 nm), suggesting exciton coupling in light of the spatial proximity of the heteroaromatic chromophores in a chiral environment.[35,36] A separate spectroscopic study was published recently that addresses this issue in more detail.[37]

Discussion

All three crystallographic structures reveal the substituted ligand in the anti conformation. In each case, the three heteroaromatic rings are tilted in the same direction with respect to the central axis of the molecule (i.e., the line containing the Zn−N_{am} bond). The magnitude of the tilt, which ranges from 7 to 26°, is influenced by several factors. No discernible trend is apparent for the effect of the substituent on the saturated carbon of the ligand arm; the average angle between the best planes of the pyridine rings and the line containing the N_{am}−Zn bond is 11.9° for $[Zn(TPA)Cl]^+$,[7] 8.3° for $[Zn(\alpha\text{-MeTPA})Cl]^+$, and 12.3° for $[Zn(\alpha\text{-PhTPA})Cl]^+$. The presence of a bulky substituent at the pyridine position-6 appears to increase this angle for $[Zn(\alpha\text{-MeBQPA})Cl]^+$ (15.9°). Overall, crystal packing forces probably account for much of the difference in magnitude of the tilt angles as seen in the fact that even in $[Zn(TPA)Cl]^+$ one of the angles is double the other two (17.2, 9.7, and 8.9°).[7] Taken together, the orientation of the rings in a complex constitutes a propeller-like twist. The sense of this twist is the same in each complex relative to the absolute configuration of the asymmetric carbon atom of the molecule.

Recently, circular dichroism studies have yielded much interesting information about solution structures,[38] so this technique was employed in an attempt to discern the behavior of the present complexes in solution. For each ligand, the Zn(Cl)(ClO_4) and Cu(Cl)(ClO_4) complexes give larger anisotropic absorptions than the free ligand. This is the expected result if the ligand adopts a similar conformation in solution as that observed in the solid state. The free ligand has many accessible conformations, so that no special chirality is present. Upon presentation of a Zn(II) or Cu(II) ion, the ligand wraps around the metal, with the heteroaromatic rings adopting a helical configuration whose sense is dictated by the absolute configuration of C_α. The reduced effect observed in the Cd(II) complexes serves as an important control experiment, since the expected octahedral $[Cd(L)I_2]$[7] complexes would place the ligand in a C_σ conformation, which would not possess the propeller-like arrangement of the heteroaromatic moieties.

The dissymmetry factor (also called optic anisotropy, $g = \Delta\epsilon/\epsilon \times 10^3$) was calculated for the ligands and complexes (Table 2). The trigonal bipyramidal complexes (Zn(II) or Cu(II)) give relatively large values, whereas the values for the free ligand and the Cd(II) complexes are small. In the case of *S*-α-MeBQPA, the Zn(II) complex has a value of 6.3 and the Cu(II) complex of 3.8 at $\lambda = 243$, both being high values for aromatic chromophores. For comparison, (+) hexahelicene presents a $g_{244} = 7.7$, and (+)-1,1′-binaphthyl-2,2′-diamine a $g_{247} = 3$.[39] In the case of *S*-α-$MePh_2TPA$, the values are somewhat lower for the Zn(II) complex ($g_{307} = 2.6$). The relatively larger effect observed for Zn(II) and Cu(II) complexes persists as it does for *R*-α-MeTPA (Zn, $g_{265} = 1.5$; Cu, $g_{265} = 1.1$).

The magnitude of the $\Delta\epsilon$ and of the *g* number increases in the order $[Zn(\alpha\text{-MeTPA})Cl]ClO_4 < [Zn(\alpha\text{-MePh}_2\text{TPA})Cl]ClO_4 < [Zn(\alpha\text{-MeBQPA})Cl]ClO_4$. This result is consistent with the observation in the crystallographic data that the tilt of the heteroaromatic rings and thus the propeller twist is larger in the quinoline containing complex than in the α-MeTPA one. Thus, the magnification of the chirality by metal ion complexation is larger when the arms contain sterically demanding substituents.

It should be noted that analysis of the spectra of the Cu(II) complexes may be complicated by the possible presence of both trigonal bipyramidal and square pyramidal complexes in solution. The absorbances at 872 and 725 nm are diagnostic of partitioning between these two coordination geometries.[17] In $[Cu(TPA)Cl]ClO_4$ (2 mM solution in methanol), the major absorbance is at 872 nm ($\epsilon = 148$) with a shoulder at 725 nm ($\epsilon = 79$). The complex $[Cu(\alpha\text{-MeTPA})Cl]ClO_4$ is nearly identical ($\epsilon = 156, 82$) while $[Cu(\alpha\text{-MeBQPA})Cl]ClO_4$ (two peaks, $\epsilon = 157, 145$) and $[Cu(\alpha\text{-MePh}_2\text{TPA})Cl]ClO_4$ (one broad peak, $\epsilon = 146, 124$) give patterns that indicate that a mixture of trigonal bipyramidal and square pyramidal geometries are present. However, the strong circular dichroic signals compared with the corresponding zinc complexes, which should adopt only trigonal bipyramidal coordination, suggests the possibility that the copper complexes might give even more intense circular dichroic signals if the coordination of the copper were more predominantly trigonal bipyramidal. The frozen EPR spectra of $[Cu(\alpha\text{-MeTPA})Cl]ClO_4$ ($g_{||} \sim 2.00$, $g_\perp = 2.19$, $A_\perp = 92 \times 10^{-4}$ cm^{-1}) and $[Cu(\alpha\text{-BQPPA})Cl]ClO_4$ ($g_{||} \sim 2.00$, $g_\perp = 2.22$, $A_\perp = 124 \times 10^{-4}$ cm^{-1}) are consistent with those for Cu(II) complexes with tripodal ligands that have trigonal bipyramidal geometry.[40]

Monte Carlo/stochastic dynamics (MC/SD) simulations of the conformational behavior of the $[Zn(L)Cl]^+$ complexes were conducted; the procedures and detailed results of the study are included in the Supporting Information. Summarizing, the simulations provided a picture of the complexes as dynamic molecules interconverting between two energetically accessible conformations (anti and syn). Energy minimization of structures generated in the MC/SD simulation resulted in only two unique structures (Λ and Δ). Under the conditions of the simulation, the two conformations interconvert rapidly but (in the α-substituted ligand complexes) with a bias for the anti conformation as anticipated from model examination and semiempirical calculations. As the two ligand conformations interconvert, the tilt of the pyridine rings and thus the axial chirality of propeller reverses. This reversal is partially but not completely concerted

---

(35) Kirschner, S. *Coor. Chem. Rev.* **1967**, *2*, 461.
(36) Crabbé, P. *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry*; Holden-Day: San Francisco, 1965.
(37) Castagnetto, J. M.; Xu, X.; Berova, N.; Canary, J. W. *Chirality* **1997**, *9*, 616.
(38) *Circular Dichroism: Principles and Applications*; Nakanishi, K., Berova, N., Woody, R. W., Eds.; VCH Publishers: New York, 1994.
(39) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994.
(40) Karlin, K. D.; Hayes, J. C.; Juen, S.; Hutchinson, J. P.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 4106.

such that all three heteroaromatic rings are tilted in the same direction most but not all of the time. Thus, the simulations support the presence of only two conformations as minimum energy structures, and suggest that these limiting conformations predominate at room temperature despite the fact that the ligand arms are conformationally mobile and able to tilt in and out of phase with the overall twist associated with the propeller-like structure.

The ^{1}H NMR spectra of the complexes provide little specific information about conformational behavior. Low-temperature spectra of [Zn(TPA)](ClO$_4$)$_2$ show a singlet for the methylene groups in CD$_3$CN at −80 °C, whereas freezing of the interconversion of the conformational enantiomers should result in AB doublets. Spectra of [Zn(α-MeBQPA)Cl](ClO$_4$) in CD$_2$Cl$_2$ as low as −90 °C failed to show any evidence that would indicate slowly interconverting conformational isomers. This latter result may result from a low population of the higher-energy conformer at low temperature or fast exchange as suggested by the mechanism of interconversion involving rotation of single bonds sequentially in each arm.[41]

Thus, the Zn(II) and Cu(II) complexes of the chiral ligands display pronounced circular dichroic spectra with amplitudes that would be expected from much more rigid molecules. The solid-state structures display propellers resulting in orientation of the heterocycle chromophores in a manner consistent with strong solution CD spectra. The MC/SD simulations connect the solid state and spectroscopic data by showing that although the arms of the tripod ligands are quite mobile, they remain in an orientation similar to that observed in the solid-state most of the time, allowing strong anisotropic absorption despite conformational mobility.

Conclusions

A combination of crystallographic, spectroscopic, and computational methods provides a consistent picture of these coordination complexes. The conformationally flexible ligands wrap around trigonal bipyramidal Zn^{II} and Cu^{II} ions, forming a propeller-like complex due to the tilt of the heterocyclic rings with respect to the central axis of the molecule. In the complex, two conformations are available with opposite axial chirality, with one being preferred. A single conformation is observed in the solid state for three complexes that have been crystallized, and a similar conformation appears to predominate in solution as the circular dichroic data attest. The MC/SD simulations provide a more detailed picture of the dynamic chirality of the complexes that is consistent with all of the observed data.

Acknowledgment. We thank the National Institutes of Health (GM 49170) for support of this research. We are grateful to Professor Donald Wink for assistance with the crystallographic structures. EI, FAB, and high-resolution mass spectra were obtained at the Michigan State University Mass Spectrometry Facility (supported in part by grant DRR-00480, from the Biotechnology Research Technology Program, NCRS, NIH).

Supporting Information Available: Molecular modeling computational procedures and results, and X-ray crystallographic details for [Zn(αMeTPA)Cl](ClO$_4$) and [Zn(α-PhTPA)Cl](ClO$_4$), including experimental procedures, positional and thermal parameters, temperature factors, bond distances and angles, and torsional angles (88 pages). Ordering information is given on any current masthead page.

IC9803098

---

[41] Recently, the minor (syn) conformer of a copper complex of ligand **2** was observed crystallographically: Xu, X.; Canary, J. W., unpublished results.