# Self-Assembly of a Triple-Stranded *meso*-Helicate from Two Iron(II) Ions and Three $[CH_2]_3$-Bridged Bis(2,2′-bipyridine) Ligands

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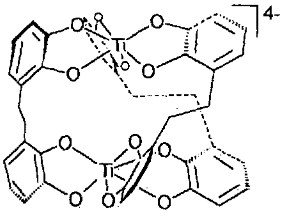
1,3-Bis(5′-methyl-2,2′-bipyrid-5-yl)propane (**3**) can be synthesized by a two-step procedure starting from 3-picoline (**1**). In a spontaneous self-assembly process **3** forms the binuclear triple-stranded *meso*-helicate $[(\mathbf{3})_3Fe_2][PF_6]_4$ on addition of iron(II) salts. The (Λ,Δ) structure can be shown by symmetry considerations based on NMR spectroscopy and is due to the conformational restrictions of the $[CH_2]_3$ spacer.

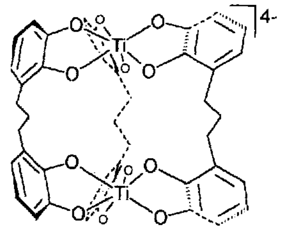
The self-assembly of linear polynuclear metal complexes became an intensely studied field of supramolecular chemistry[1]. Thus, the use of linear oligodentate nitrogen donor ligands and soft metal ions led to a number of double-[2] and triple-stranded helicates[3,4] with two or more metal centers. Besides the chiral helicates, achiral "face-to-face" complexes could be observed in the case of the double-stranded systems[5].

For binuclear triple-stranded complexes two diastereomeric forms are possible. On the one hand the coordination compound can exhibit the traditional helicate structure (type I). This helicate contains two propeller-type[6] complex units which both possess the same helical twist[7]. If the two metal centers show opposite configuration, the corresponding *meso* form is obtained. This achiral complex contains two propeller type helical portions which possess an opposite twist and consequently should be termed *meso*-helicate. This is a similar case as observed for tartaric acid. In chiral (D/L) tartaric acid both chiral centers are equally configurated. In the *meso* form the two chiral subunits (central chirality!) of the tartaric acid possess opposite configuration. Due to this difference chiral and meso tartaric acid show a different spatial arrangement[8]. In the case of the helicate versus the *meso*-helicate a very similar situation is observed for the chiral subunits which now possess helical chirality. The resulting *meso*-helicate has no longer a helical structure but is made of two small helical building blocks (or propellers) with a different helical twist.

With nitrogen donor ligands only the chiral helicate could be obtained. However, recently we could show that alkyl-bridged bis(catecholate) ligands and hard metal ions [e.g. titanium(IV)] selectively form triple-stranded *meso*-helicates as well as traditional helicates[9]. Thus, the stereochemistry of the self-assembly process of the achiral components can be controlled by the use of conformationally constrained spacers between the chelating units. In the case of alkyl spacers the conformational restrictions are introduced by the preferential formation of a zigzag chain. If the chelating units and the connected benzylic methylene groups are orientated in a linear arrangement, a different ligand orientation is obtained for systems with odd or even chain length. Ligands with an even number of methylene units in the spacer lead to the formation of chiral helicates (type I). With an odd number of methylene units the achiral *meso*-helicate (type II) is obtained[9].



helicate
(Δ,Δ-form)
type *I*



*meso*-helicate
(Δ,Λ-form)
type II

The results with oxygen donor ligands made us wonder why no triple-stranded *meso*-helicate-type compounds were obtained with nitrogen donor systems. For the self-assembly of linear triple-stranded oligonuclear metal complexes mainly spacers with even chain length are described in the literature[4]. In the few cases where an odd spacer length was chosen, either sp$^2$ centers were introduced in the chain disturbing the zigzag conformation[3,10] or the spacer was attached to the chelating moiety in such a position that a linear orientation of the ligand was prevented[3,11]. We decided to examine whether the influence of the chain length is transferable to e.g. bis(2,2′-bipyridine) ligands.

In this paper we present a facile synthesis of a $[CH_2]_3$-bridged bis(2,2′-bipyridine) ligand which, by self-assembly, forms a triple-stranded *meso*-helicate with iron(II).

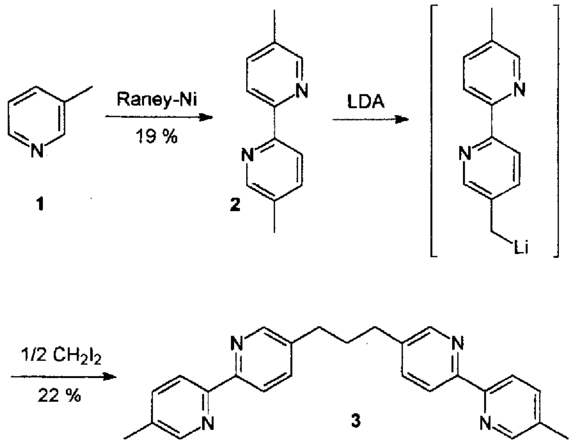
## Results and Discussion

### Ligand Synthesis

1,3-Bis(5′-methyl-2,2′-bipyrid-5-yl)propane (**3**) was obtained by a two step procedure as depicted in Scheme 1.

Starting with 3-methylpyridine (3-picoline, **1**) we obtained, as described by Sasse and Vögtle[12], 5,5′-dimethyl-2,2′-bipyridine (**2**) in 19% yield.

Scheme 1



Reaction of **2** with LDA led to the corresponding benzyllithium derivative[4]. Subsequent addition of half an equivalent of diiodomethane afforded the bis(2,2′-bipyridine) ligand **3** in 22% yield as a white solid. In the $^1$H-NMR spectrum ([D]chloroform) **3** displays characteristic signals for the 2,2′-bipyridine moieties at δ = 8.47 (m, 4H), 8.24 (m, 4H), and 7.59 (m, 4H) and for the spacer at δ = 2.70 (t, *J* = 7.6 Hz, 4H) and 2.00 (quint, *J* = 7.6 Hz, 2H). The signal of the methyl groups is observed at δ = 2.35 (s, 6H).

### Coordination Studies

The binuclear octahedral iron(II) low-spin complex was prepared by addition of a solution of $Fe(SO_4) \cdot 7\ H_2O$ (2 equiv.) in water to ligand **3** (3 equiv.) in ethanol. The mixture immediately turned dark red and was refluxed for two hours. After removal of the solvent the residue was dissolved in a small amount of water and precipitated by addition of aqueous $[NH_4][PF_6]$. Recrystallization from acetone/ether provided $[(\mathbf{3})_3Fe_2][PF_6]_4$ in 88% yield as a dark red crystalline solid. The perchlorate salt $[(\mathbf{3})_3Fe_2][ClO_4]_4$ was synthesized similarly in 82% yield[13].

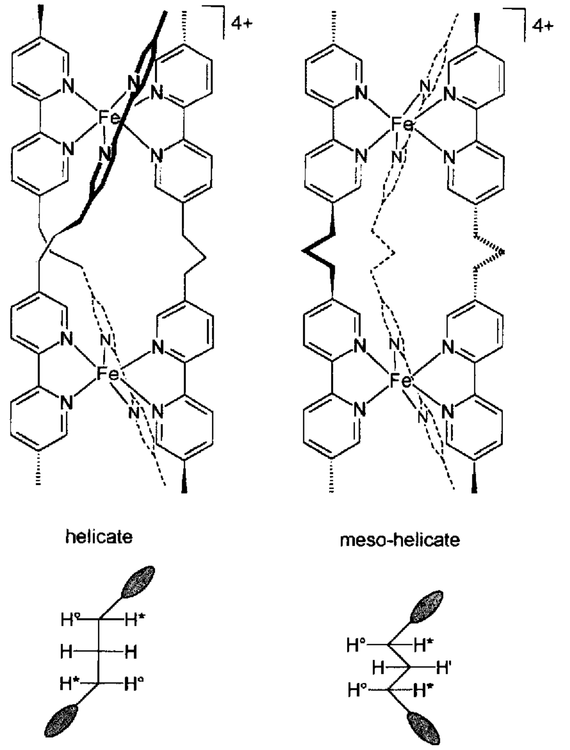
Scheme 2

$$3\ \mathbf{3}\ \xrightarrow[91\ \%]{1)\ 2\ Fe(SO_4)\cdot 7H_2O\quad 2)\ [NH_4][PF_6]}\ [(3)_3Fe_2][PF_6]_4$$

The composition of the binuclear tris(ligand) complex was determined by mass spectrometry. The FAB(+) mass spectrum (3-nitrobenzyl alcohol as matrix) exhibited a peak of $[(\mathbf{3})_3Fe_2][PF_6]_3{}^+$ at *m/z* = 1688 (correct isotopic pattern). The corresponding peak of $[(\mathbf{3})_3Fe_2][ClO_4]_3{}^+$ is observed at *m/z* = 1552.

The $^{13}$C-NMR spectrum ([D$_6$]acetone, 125 MHz, 296 K) displays only one set of signals for the aromatic ligands of $[(\mathbf{3})_3Fe_2][PF_6]_4$ at δ = 159.6 (C), 158.3 (C), 155.7 (CH), 153.4 (CH), 143.8 (C), 141.0 (CH), 140.9 (CH), 139.8 (C), 125.2 (CH), and 125.0 (CH). Additionally, the resonance of the methyl group at δ = 19.3 and the signals of the methylene groups of the spacer are observed at δ = 38.2 and 34.2 (double intensity). The simplicity of the spectrum shows that the metal complex possesses a high symmetry and adopts only one of the diastereomeric structures which are depicted in Figure 1.

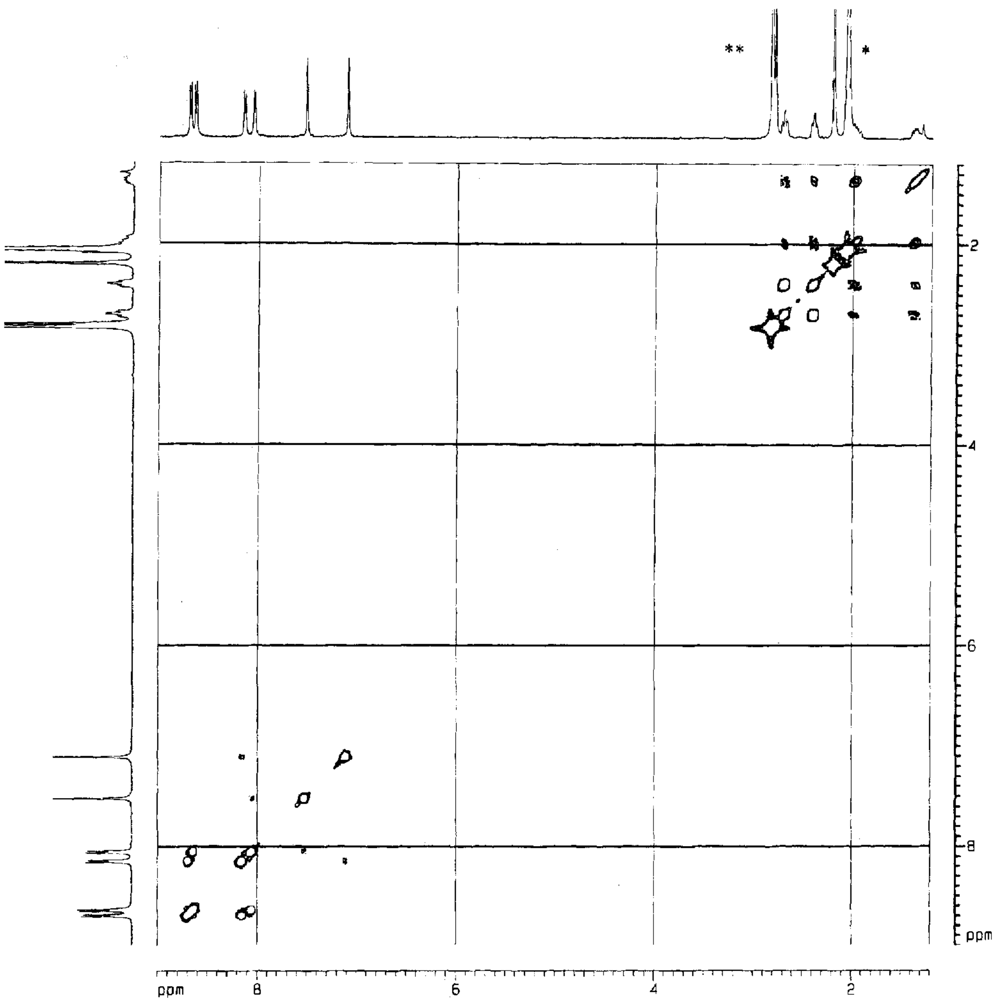
Figure 1. Representation of the structure of $[(\mathbf{3})_3Fe_2]^{4+}$ as helicate or *meso*-helicate and schematic view of one of the ligand strands



The structure of the chiral helicate or the achiral *meso*-helicate form was determined by $^1$H-NMR spectroscopy ([D$_6$]acetone, 500 MHz, 296 K). In Figure 1 the helicate and the *meso*-helicate structure of $[(\mathbf{3})_3Fe_2]^{4+}$ and the schematic presentation of one ligand strand of the diastereoisomers is shown. Due to the chirality of the octahedrally coordinated metal centers in both cases the benzylic protons should show a diastereotopic behavior and thus should give rise to two sets of signals. However, the central methylene group can act as a probe to distinguish between the helicate and the *meso*-helicate form[9]. In the chiral helicate only one signal should be observed for the protons of this group (the two protons are related by $C_2$ symmetry). The *meso*-helicate should possess two diastereotopic protons and thus its spectrum should exhibit two sets of signals.

In the $^1$H-NMR spectrum of $[(\mathbf{3})_3Fe_2][PF_6]_4$ the signals of the 2,2′-bipyridine ligand moieties are observed at δ = 8.70 (d, *J* = 8.2 Hz, 6H), 8.64 (d, *J* = 8.2 Hz, 6H), 8.15 (d, *J* = 8.2 Hz, 6H), 8.06 (d, *J* = 8.2 Hz, 6H), 7.52 (s, 6H), and 7.11 (s, 6H). A singlet for the methyl group is found at δ = 2.20 (s, 18H). The $[CH_2]_3$ spacers give rise to two sig-

Figure 2. COSY spectrum ([D$_6$]acetone, 500 MHz, 296 K) of [(3)$_3$Fe$_2$][PF$_6$]$_4$ (* = [D$_5$]acetone; ** = water)



nals for the diastereotopic protons in the benzylic position at δ = 2.71 (m, 6H) and 2.40 (m, 6H) and to two signals for the protons of the central methylene group at δ = 2.0 (m, partly hidden under the solvent peak) and 1.40 (m, 3H). Additionally, the existence of the multiplet at δ = 2.0 was confirmed by a COSY NMR spectrum (Figure 2) which clearly shows the coupling between the four different groups of protons of the spacer.

The occurrence of two sets of signals for the protons of the central methylene unit proves unambiguously that [(3)$_3$Fe$_2$][PF$_6$]$_4$ adopts the *meso*-helicate structure. Thus, we can control the stereochemistry of the self-assembly process of linear nitrogen donor ligands in the same way as we have shown for the corresponding oxygen donor systems. The concept of stereocontrol by use of simple conformational restrictions in achiral components opens up new possibilities in stereoselective (metallo)supramolecular chemistry[14].

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## Experimental

Melting points (uncorrected): Büchi 535. – IR: Bruker IFS. – MS: Finnigan MAT 90. – UV-Vis: Perkin Elmer UV-Vis LAMBDA 2. – $^1$H NMR and $^{13}$C NMR (BB/DEPT): Bruker DRX 500, AM 400, or WM 250, T = 296 K; internal standard: chloroform or [D$_5$]acetone. – All reactions were carried out under argon.

*Synthesis of 5,5'-Dimethyl-2,2'-bipyridine* (**2**): **2** was obtained from 3-picoline (**1**) as described by Sasse and Vögtle[12] in 19% yield as yellow crystals; m.p. 115°C (ref.[12] 114–116°C). – $^1$H NMR (CDCl$_3$, 400 MHz): δ = 8.45 (br. s, 2H, CH), 8.20 (d, $J$ = 7.8 Hz, 2H, CH), 7.56 (d, $J$ = 7.8 Hz, 2H, CH), 2.33 (s, 6H, CH$_3$). – $^{13}$C NMR (CDCl$_3$, 100 MHz): δ = 153.7 (C), 149.5 (CH), 137.3 (CH), 132.9 (C), 120.2 (CH), 18.3 (CH$_3$).

*Synthesis of 1,3-Bis(5'-Methyl-2,2'-bipyrid-5-yl)propane* (**3**)[15]: Diisopropylamine (0.7 ml, 5 mmol) was dissolved in 10 ml of THF and at 0°C a 1.6 M solution of *n*BuLi in hexane (3.1 ml, 4.96 mmol) was added. After 15 min the mixture was cooled to −78°C and a solution of **2** (0.92 g, 5 mmol) in 10 ml of THF was slowly added. After the addition was complete the solution was allowed to warm to room temp.[4]. Diiodomethane (670 mg, 2.5 mmol) was added and the mixture was stirred for 14 h. The solvent was removed and the residue extracted with water/dichloromethane. After separation and drying ($MgSO_4$) of the organic phase the solvent was removed. The residue was purified by column chromatography (ALOX-N, hexane/ethyl acetate, 5:1 → 3:1) to afford 206 mg (0.54 mmol, 22%) of **3** as a white solid; m.p. 172 °C. – $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ = 8.47 (m, 4H, CH), 8.24 (m, 4H, CH), 7.59 (m, 4H, CH), 2.70 [t, $J$ = 7.6 Hz, 4H, $CH_2$ (benzylic)], 2.35 (s, 6H, $CH_3$), 2.00 [quint, $J$ = 7.6 Hz, 2H, $CH_2$ (central)]. – $^{13}C$ NMR ($CDCl_3$, 63 MHz): $\delta$ = 154.3 (C), 153.6 (C), 149.6 (CH), 149.2 (CH), 137.5 (CH), 136.8 (CH), 133.1 (C, double intensity), 120.5 (CH), 120.4 (CH), 32.2 ($CH_2$), 32.1 ($CH_2$, double intensity), 12.4 ($CH_3$). – IR (KBr): $\tilde{\nu}$ = 3086 ($CH_{aryl}$), 2939, 2920 ($CH_{alkyl}$), 1470 (CH), 826. – MS (EI, 70 eV): $m/z$ (%) = 380 (65) $[M]^+$, 197 (21) $[C_{13}H_{14}N_2]^+$, 184 (100) $[C_{12}H_{12}N_2]^+$. – $C_{25}H_{24}N_4$ (380.5): calcd. C 78.92, H 6.36, N 14.73; found C 78.56, H 6.45, N 14.32.

*Synthesis of* $[(\mathbf{3})_3Fe_2][PF_6]_4$: $FeSO_4 \cdot 7\ H_2O$ (31.2 mg, 0.112 mmol) in 2 ml of water was added to a solution of **3** (64.0 mg, 0.168 mmol) in ethanol. The dark red solution was heated at reflux (2 h) and solvent removed in vacuo. The remaining solid was dissolved in a small amount of water and precipitated as the $PF_6$ salt by addition of $[NH_4][PF_6]$ (50 mg, 0.3 mmol) in 5 ml of water. The crude product was recrystallized from acetone/ether to furnish $[(\mathbf{3})_3Fe_2][PF_6]_4 \cdot 3\ H_2O$ (93 mg, 88%) as dark red crystals; m.p. 248 °C (dec.). – $^1H$ NMR ([$D_6$]acetone, 500 MHz): $\delta$ = 8.70 (d, $J$ = 8.2 Hz, 6H, CH), 8.64 (d, $J$ = 8.2 Hz, 6H, CH), 8.15 (d, $J$ = 8.2 Hz, 6H, CH), 8.06 (d, $J$ = 8.2 Hz, 6H, CH), 7.52 (s, 6H, CH), 7.11 (s, 6H, CH), 2.71 [m, 6H, CH (benzylic)], 2.40 [m, 6H, CH (benzylic)], 2.20 (s, 18H, $CH_3$), 2.0 [m, CH (central) partly hidden under solvent peak], 1.40 [m, 3H, CH (central)]. – $^{13}C$ NMR ([$D_6$]acetone, 125 MHz): $\delta$ = 159.6 (C), 158.3 (C), 155.7 (CH), 153.4 (CH), 143.8 (C), 141.0 (CH), 140.9 (CH), 139.8 (C), 125.2 (CH), 125.0 (CH), 38.2 ($CH_2$), 34.6 ($CH_2$, double intensity), 19.3 ($CH_3$). – IR (KBr): $\tilde{\nu}$ = 3044 ($CH_{aryl}$), 2929, 2867 ($CH_{alkyl}$), 1477 (CH), 842 (PF). – UV/Vis (acetone): $\lambda_{max.}$ ($\varepsilon$) = 312 (114600), 354 (12200), 514 (16800), shoulder near 475 nm. – FAB(+) MS (3-nitrobenzyl alcohol): $m/z$ = 1688 ($[(\mathbf{3})_3Fe_2][PF_6]_3^+$, correct isotopic pattern). – $C_{75}H_{72}N_{12}F_{24}Fe_2P_4 \cdot 3\ H_2O$ (1887.1): calcd. C 47.74, H 4.17, N 8.91; found C 47.59, H 3.34, N 8.62.

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[1] Reviews: E. C. Constable, *Tetrahedron* **1992**, *48*, 10013; *Progr. Inorg. Chem.* **1994**, *42*, 67; C. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725; J.-M. Lehn, *Supramolecular Chemistry – Concepts and Perspectives*, VCH, Weinheim, **1995**, and references cited therein.

[2] J.-M. Lehn, A. Rigault, *Angew. Chem.* **1988**, *100*, 1121; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1095; E. C. Constable, A. J. Edwards, P. R. Raithby, J. V. Walker, *Angew. Chem.* **1993**, *105*, 1486; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1465; K. T. Potts, M. Keshavarz-K, F. S. Tham, H. D. Abruna, C. Arana, *Inorg. Chem.* **1993**, *32*, 4450.

[3] A. F. Williams, C. Piguet, G. Bernardinelli, *Angew. Chem.* **1991**, *103*, 1530; *Angew. Chem. Int. Ed. Engl.* **1991**, *103*, 1530; K. T. Potts, C. P. Horwitz, A. Fessak, M. Keshavarz-K, K. E. Nash, P. J. Toscano, *J. Am. Chem. Soc.* **1993**, *115*, 10444; R. C. Scarrow, D. L. White, K. N. Raymond, *J. Am. Chem. Soc.* **1985**, *107*, 6540; E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1995**, *107*, 1082; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 996; for the resolution of a triple-stranded helicate, see e.g.: L. J. Charbonnière, M.-F. Gilet, K. Bernauer, A. F. Williams, *J. Chem. Soc. Chem. Commun.* **1996**, 39.

[4] R. Krämer, J.-M. Lehn, A. De Cian, J. Fischer, *Angew. Chem.* **1993**, *105*, 764; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 703; M. T. Youinou, R. Ziessel, J.-M. Lehn, *Inorg. Chem.* **1991**, *30*, 2144; R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394.

[5] S. Rüttimann, C. Piguet, G. Bernardinelli, B. Boquet, A. F. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 4230; A. Bilyk, M. M. Harding, P. Turner, T. W. Hambley, *J. Chem. Soc. Dalton Trans.* **1994**, *2783*; C. O. Dietrich-Buchecker, J.-P. Sauvage, J.-P. Kintzinger, P. Maltese, C. Pascard, J. Guilhem, *New J. Chem.* **1992**, *16*, 931.

[6] A propeller is obtained when a helix is reduced to the smallest possible chiral unit, e.g.: E. L. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley New York **1994**, pp. 1156–1166.

[7] An octahedral metal complex with three bidentate ligands adopts the shape of a propeller and thus is a smallest possible helical unit, e.g.: K. P. Meurer, F. Vögtle, *Top. Curr. Chem.* **1985**, *127*, 1; F. Vögtle, *Supramolekulare Chemie*, Teubner Studienbücher Stuttgart **1992**, p. 130; J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry*, 4th ed., Harper Collins, New York, **1993**, p. 495.

[8] Ref.[6], pp. 65–67.

[9] M. Albrecht, S. Kotila, *Angew. Chem.* **1995**, *107*, 2285; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2134; M. Albrecht, S. Kotila, *Angew. Chem.*, in press; M. Albrecht, H. Röttele, P. Burger, submitted for publication.

[10] S. L. Larson, S. M. Hendrickson, S. Ferrere, D. L. Derr, C. M. Elliott, *J. Am. Chem. Soc.* **1995**, *117*, 5881; see also: B. R. Serr, K. A. Andersen, C. M. Elliott, O. P. Anderson, *Inorg. Chem.* **1988**, *27*, 4499.

[11] D. Zurita, P. Baret, J.-L. Pierre, *New J. Chem.* **1994**, *18*, 1143.

[12] W. H. F. Sasse, *J. Chem. Soc.* **1959**, 3046; W. H. F. Sasse, C. P. Whittle, *J. Chem. Soc.* **1961**, 1347; F. Ebmeyer, F. Vögtle, *Chem. Ber.* **1989**, *122*, 1725.

[13] M. Albrecht, C. Riether, *Synlett* **1995**, 309.

[14] For further examples of diastereoselectivity in self-assembly processes, see e.g.: J. H. Small, D. J. McCord, J. Greaves, K. J. Shea, *J. Am. Chem. Soc.* **1995**, *117*, 11588; R. W. Saalfrank, B. Hörner, D. Stalke, J. Salbeck, *Angew. Chem.* **1993**, *105*, 1223; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1179.

[15] Ligand **3** was independently synthesized by a different procedure: A. von Zelewsky, P. Belser, personal communication; J. A. Nachbaur, PhD Thesis, University of Fribourg (Switzerland), **1993**.

[96007]