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Article

Formation of Racemate and Mesocate Complexes from an Achiral Tripodal Ligand Containing Three Benzimidazole Groups

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Two complexes of the achiral tripodal ligand tris(1-benzimidazolylethyl)amine (nteb), viz., $[Mn(nteb)_2(H_2O)_2](ClO_4)_2 \cdot CH_3OH$, **1**, and $[Ag_2(nteb)_2](CF_3CO_2)_2 \cdot 2H_2O$, **2**, have been synthesized and characterized by IR, ^{1}H NMR, and EPR spectroscopy (**1**), electrospray mass spectrometry, thermogravimetric analysis, and X-ray crystallography. Compound **1** contains chiral complex cations due to the same handedness of two nteb ligands ($\delta\delta$ or $\lambda\lambda$) but crystallizes as a racemate, while **2** contains a dinuclear mesocate because of the opposite handedness ($\delta\lambda$) of two nteb ligands. Crystal data for **1**: space group $P\bar{1}$ with $a = 9.471(4)$ Å, $b = 16.884(7)$ Å, $c = 19.906(8)$ Å, $\alpha = 77.930(7)°$, $\beta = 88.063(7)°$, $\gamma = 89.706(7)°$, $V = 3111(2)$ Å^3, and $Z = 2$. Crystal data for **2**: space group $P\bar{1}$ with $a = 9.3390(12)$ Å, $b = 10.2168(13)$ Å, $c = 16.382(2)$ Å, $\alpha = 75.721(3)°$, $\beta = 87.857(3)°$, $\gamma = 71.738(3)°$, $V = 1437.2(3)$ Å^3, and $Z = 1$. In **1**, water serves as an auxiliary ligand, connected to one imidazole N atom of each nteb ligand through a H-bridge; the cationic complexes are associated intermolecularly via $\pi\cdots\pi$ interactions. In contrast to **1**, the coordination to the Ag^+ ions in **2** occurs in a heterochiral manner and produces a dinuclear mesocate.

Introduction

Compared with the extensively studied asymmetric synthesis in organic chemistry, the interest in inorganic stereochemistry has not drawn much attention until recently.[1] This may be due to the fact that the chirality of coordination compounds is more complicated because of the variety of possible central atoms and their variable coordination geometries; in addition, chiral predetermination can be achieved by induction from a given chirality in the ligand sphere to produce a preferred chirality at the metal center.[2] For instance, chiral C_3-symmetric ligands are of current interest for use in asymmetric catalysis and chiral recognition since they may reduce the number of possible diastereomeric intermediates or transition states by the 3-fold rotational symmetry element.[3] On the other hand, the formation of chiral assemblies from achiral species is a burgeoning field which has advanced to the stage of supramolecular chirality.[4] Helical assemblies have long been the best recognized examples in this field.[5] In addition to helical structures constituted by one or more covalent organic strands, the

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"molecular propeller" arrangement which possesses two or more subunits as "blades" radiating from an axis of rotation (the propeller axis) represents an interesting topic.[6] Achiral molecules with C_3 symmetry have been employed to construct both organic[6] and inorganic[7] chiral structures.

Previous studies of metal complexes with tripodal ligands[8] revealed that two C_3-symmetric ligands such as tris(2-benzimidazolylmethyl)amine (ntb) or its alkyl-substituted derivatives, the tris(*N*-R-benzimidazol-2-ylmethyl)amines (Rntb), can encapsulate one or more metal ions with the two tripodal ligands exhibiting "double"-propeller-like topology (each tripodal ligand exhibiting an independent propeller sense). With lanthanide(III) ions, spontaneous resolution of the homochiral crystals may occur during crystallization,[8b] or the chiral coordination motifs can act as hydrogen donor building blocks toward 4,4′-bipyridine or (*E*)-1,2-bis(4-pyridyl)ethylene to generate doubly interpenetrating 3D stereoisomeric networks.[7c] Herein a more flexible C_3-symmetrical ligand, tris(1-benzimidazolylethyl)amine (nteb), was employed to obtain two remarkable complexes, viz., $[Mn(nteb)_2(H_2O)_2](ClO_4)_2 \cdot CH_3OH$, **1**, and $[Ag_2(nteb)_2](CF_3CO_2)_2 \cdot 2H_2O$, **2**. The former is chiral due to the same clockwise ($\delta\delta$)[9] or anticlockwise ($\lambda\lambda$)[9] arrangement of two tripodal ligands, the enantiomers cocrystallizing as a racemate. The latter can be described as a mesocate because of the opposite arrangement ($\delta\lambda$)[9] of the two ligands. Such chiral features are comparable to those of dinuclear triple-stranded helicate-type complexes in which helicate and mesocate forms are well documented.[10]

Results and Discussion

Syntheses. The tripodal ligand nteb is readily prepared in a substitution reaction of tris(2-chloroethyl)amine with 1*H*-benzimidazole as shown in Scheme 1. It differs from the related ntb ligand by containing longer ethylene spacers connecting the three benzimidazolyl arms to the amine N atom. Therefore, nteb was expected to form sandwich structures rather than encapsulate one or more metal ions.[8] Reaction of $Mn(ClO_4)_2 \cdot 6H_2O$ or $AgCF_3CO_3$ with nteb in MeCN−MeOH (v/v 1:2) solution led to the isolation of complexes **1** and **2** consistent with the results of elemental analyses and confirmed by X-ray crystallography.

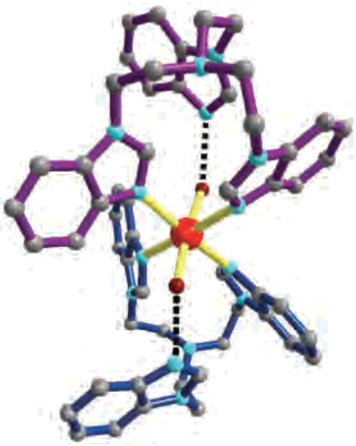
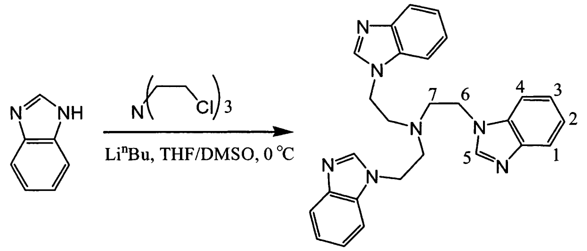


Figure 1. Representation of the $[Mn(nteb)_2(H_2O)_2]^{2+}$ cation in **1** (Λ enantiomer). Key: Mn (red), C (gray), N (cyan), O (dark red). The two ligands are distinguished by different colors of bonds.

Scheme 1



Crystal Structures. The crystal structure of **1** consists of one $[Mn(nteb)_2(H_2O)_2]^{2+}$ cation, one methanol molecule, CH_3OH, and two free ClO_4^- anions. As depicted in Figure 1, the coordination geometry of the Mn^{2+} ion in **1** can be described as close to octahedral. The Mn^{2+} ion is bonded to four imine nitrogen atoms of four benzimidazole arms from two nteb ligands, and to two oxygen atoms from water molecules. The coordinated nitrogen atoms are coplanar to constitute an equatorial plane, while the two water oxygen atoms are located in the axial positions. The Mn−N (2.261(2)−2.323(2) Å) and Mn−O (2.1632(18) and 2.2082(18) Å) distances are comparable with those found in related manganese(II) complexes.[11] The remaining benzimidazole arm of each nteb ligand is not directly involved in metal coordination because of steric hindrance but is connected to the axial water molecule via hydrogen bonding (N7···O2 2.687 Å, N10···O1 2.718 Å). In effect, two composite tridentate N,N,O-ligands $[nteb \cdot H_2O]$ are coordinated in *fac* configuration to the Mn^{2+} ion in **1**, the imidazole $N/H_2O/M^{2+}$ binding motif being familiar from protein structures.

By contrast, all three benzimidazole arms of the nteb ligands participate directly in metal coordination in com-

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(9) For simplicity, the propeller arrangement of the ligand is represented by the symbols δ and λ: When the ligand is viewed from the apical N atom down to three benzimidazolyl "blades", the clockwise orientation is termed as δ, while the anticlockwise orientation is termed as λ. Consequently, the chirality of the complex formed by two clockwise−clockwise ($\delta\delta$) arranged ligands is assigned as Δ, while that by two anticlockwise−anticlockwise ($\lambda\lambda$) arranged ligands is assigned as Λ. A combination of clockwise−anticlockwise ($\delta\lambda$) arrangement results in a mesocate.

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Figure 2. Representation of the $[Ag_2(nteb)_2]^{2+}$ cation in **2** (mesocate). Key: Ag (red), C (gray), N (cyan). The two ligands are distinguished by different colors of bonds.

pound **2**. To avoid spatial congestion, a dinuclear species, $[Ag_2(nteb)_2]^{2+}$, is formed besides two free $CF_3CO_2^-$ anions and two lattice H_2O water molecules in the unit cell. As shown in Figure 2, two nteb ligands are joined by two Ag^+ ions to give a sandwich structure. Each Ag^+ ion is coordinated by two benzimidazole arms of one nteb ligand and by one benzimidazole arm of the other, resulting in a "T"-shape coordination geometry with two shorter Ag−N distances of 2.138(3) and 2.184(4) Å and one relatively long distance of 2.416(4) Å ("2 + 1" coordination[12]).

The most remarkable features of the two structures come from the fact that the achiral tripodal nteb ligands exhibit a propeller-type topology. Such an arrangement is intrinsically chiral, being able to induce chirality of the complexes.[7] However, since there are two face-to-face tripodal ligands in one complex, the chirality of the resulting compound will depend on the mutual propeller orientation of the two ligands (double-propeller molecule). They can be clockwise−clockwise ($\delta\delta$), anticlockwise−anticlockwise ($\lambda\lambda$), or clockwise−anticlockwise ($\delta\lambda$). The first two homochiral forms constitute a pair of enantiomers, while the heterochiral one is an achiral *meso* structure which we can term a mesocate. Such behavior closely resembles that found for dinuclear triple-stranded helicates: Two homochiral metal centers result in a chiral helicate,[10] while two heterochiral metal centers give a mesocate.[10,13] The present two structures demonstrate exactly the formation of two such diastereoisomers with the chirality originating from the ligands instead of the metal centers. In **1** the two nteb ligands show the same right- or left-handed propeller appearance ($\delta\delta$ or $\lambda\lambda$) when the molecule is viewed down the pseudo-C_3 axis from either tertiary nitrogen atom N1 or N8 to the Mn^{2+} ion in opposite directions; thus, a chiral complex is formed. However, since the ligand itself is achiral, the chelation to the Mn^{2+} ion is expected to produce equal amounts of enantiomers of $[Mn(nteb)_2(H_2O)_2]^{2+}$ in solution as shown in Scheme 2. The crystal structural analysis shows that each type of the two enantiomers is connected by offset $\pi\cdots\pi$ interactions between adjacent enantiomers: Two nteb ligands of each enantiomer provide two benzimidazole rings to form slipped $\pi\cdots\pi$ interactions with two neighboring enantiomers [the centroid-to-centroid distance (d) and corresponding interplanar angle (τ) being about 4.2 Å and 26°, respectively], thus generating an infinite homochiral chain (ΔΔΔΔΔ... or ΛΛΛΛΛ...). Two such chains with opposite handedness are further associated via intermolecular π⋯p interactions (at $d = 3.8$ Å and $\tau = 0°$) to give an ordered two-dimensional heterochiral layer ([ΔΔΔΔΔ...][ΛΛΛΛΛ...]) in the (011) plane as shown in Figure 3. The separation between adjacent layers is about 16.8 Å, leaving a 4.3 Å wide channel to accommodate the perchlorate anions and solvated methanol molecules.

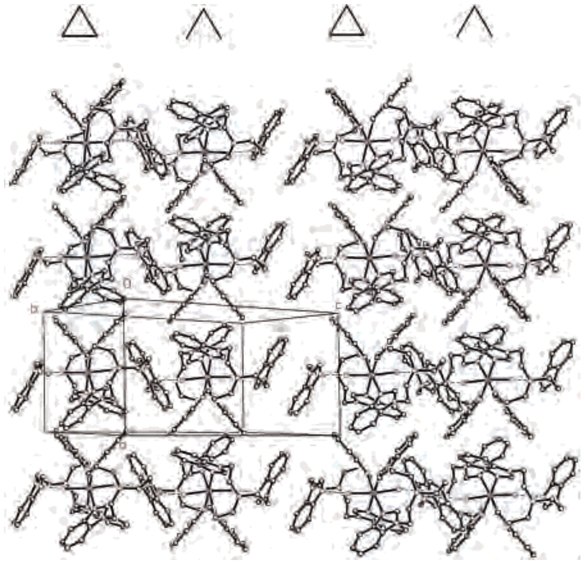
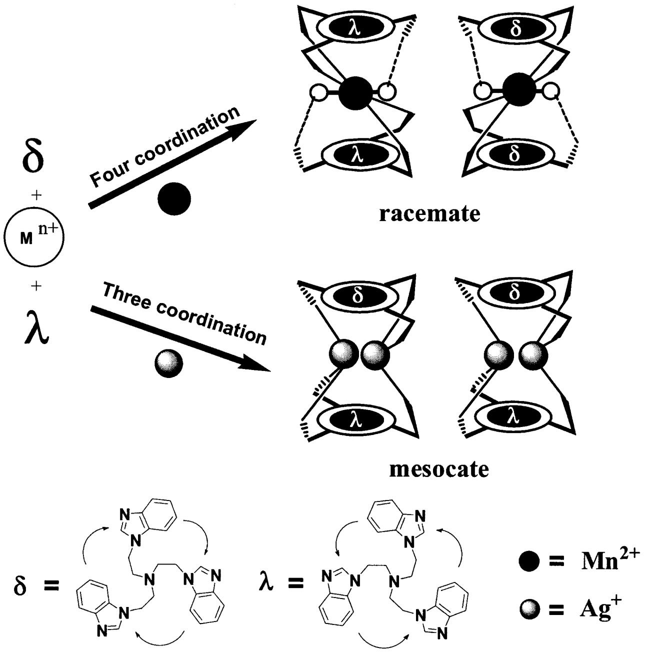


Figure 3. $[Mn(nteb)_2(H_2O)_2]^{2+}$ enantiomers arranged in alternate rows via slightly offset $\pi\cdots\pi$ interactions, forming a racemic layer in complex **1**.

Scheme 2



In contrast, two nteb ligands in the dications of dinuclear **2** adopt an opposite "screw" coordination arrangement: One is clockwise (δ) while the other is anticlockwise (λ) oriented,

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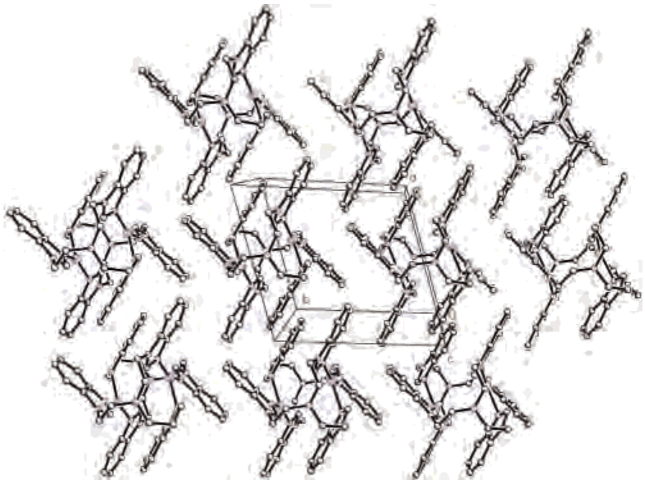

Figure 4. Two-dimensional layer of $[Ag_2(nteb)_2]^{2+}$ assembled via face-to-face $\pi\cdots\pi$ and edge-to-face $C-H\cdots\pi$ interactions.

being related by a crystallographically imposed inversion center lying between two Ag^+ ions. Therefore, the complex itself becomes a mesocate just like the dinuclear triple-stranded mesocates with two heterochiral metal centers as shown in Scheme 2.[10] The extended structure exhibits layers separated by 16.4 Å with 4.2 Å wide channels, occupied by the $CF_3CO_2^-$ anions and water molecules, similarly as in **1** (Figure 4). However, the layers in **2** are constructed by parallel aligned chains linked via face-to-face $\pi\cdots\pi$ and edge-to-face $C-H\cdots\pi$ interactions between the benzimidazole rings of adjacent $[Ag_2(nteb)_2]^{2+}$ mesocates ($\pi\cdots\pi$ interactions, $d = 3.5-3.7$ Å, $\tau = 0-18°$; $C-H\cdots\pi$ interactions, $H\cdots\pi$ 2.8−3.1 Å, $C-H\cdots\pi$ 103−112°).

It is known that achiral components can be assembled into homochiral complexes under appropriate conditions,[4,7] however, mesocates are inherently possible because of the absence of absolute chirality. Both single-stranded[14] and triple-stranded[10,13] helical structures have been found to exhibit mesocates, and many factors such as the rigidity of the ligand, the length of alkyl spacers, the presence of guest molecules, or chiral substituents can determine whether dinuclear triple-stranded helicates adopt a helical or a mesocate configuration.[10] The present double-propeller molecule can be alternatively regarded as a triple-stranded helix with a metal linking the two halves of the helical strands. The mesocate **2** is formed because the Ag^+ ions represent the point of contraflection to join both the right- and left-handed strands. The stereochemistry of such a system may also be influenced by various contributions. In complexes **1** and **2** the counteranions are not involved in the coordination, and as a consequence, the propeller sense of the two nteb ligands may be directed by the metal ions. In contrast to the *ortho* arrangement of nitrogen donor atoms and methylene spacers for each benzimidazole arm of the ntb ligand, the *meta* disposition of donor N and ethylene spacers makes it very difficult for the three benzimidazole arms of nteb to bind to one metal ion, thereby facilitating sandwich structures with two ligands linked by two or more connectors. In any case, the benzimidazole arms from two different ligands which are connected by the same connector (metal ion) should be tilted away from each other to avoid head-to-head $H\cdots H$ interference. In the present two cases, the Mn^{2+} ion prefers a higher coordination number relative to the Ag^+ ion; therefore, four benzimidazole arms of two ligands are connected by one Mn^{2+} ion in **1**. The third arm of each ligand is not able to bind to the Mn^{2+} ion because of the steric hindrance. Instead, two water molecules occupy the remaining two opposite axial positions to form $O-H\cdots N$ hydrogen bonds, directing the orientation of the third benzimidazole ring. Theoretically, the four benzimidazole arms bound to the Mn^{2+} ion can twist in either direction to avoid head-to-head $H\cdots H$ interference between two pairs of arms from the two ligands, the two ligands can then adopt either a same-handed ($\delta\delta$ or $\lambda\lambda$) or an opposite-handed ($\delta\lambda$) helical arrangement. However, only when the two ligands take the same-handed arrangement can both third arms have the chance to form hydrogen bonds to the two water molecules. Otherwise, one of the two arms has to stay away because of steric requirements as is evident from the solid-state structural analysis. The linear $O-Mn-O$ motif thus determines the propeller appearance of the two ligands to give a homochiral complex, **1**. On the contrary, each Ag^+ ion in **2** connects three benzimidazole arms of *two* ligands which are centrosymmetrically related. The orientation of each benzimidazole arm is controlled by Ag^+, and only an opposite-handed ($\delta\lambda$) arrangement of the two ligands can effectively avoid $H\cdots H$ interference between each pair of arms from the two ligands. Therefore, different coordination modes of Mn^{2+} and Ag^+ account for the different propeller senses of the two ligands, resulting in either homochiral **1** or mesocate **2**.

Spectroscopic Studies. To investigate the solution structure, ^1H NMR spectra were recorded for both complexes and the free ligand. The broad proton signals in the spectrum of **1** indicate the presence of paramagnetic manganese(II). This was confirmed by EPR, which showed the normal six-line splitting ($I = 5/2$ of ^{55}Mn) at $g = 2.0023$ with a coupling constant of 94.5 G. By contrast, the ^1H NMR spectrum of **2** exhibits one set of proton signals which are better resolved even than those of the free ligand nteb as shown in Figure 5. All signals except one are downfield shifted (0.06−0.31 ppm), indicative of complexation. The most remarkable finding is that the proton signal of H_5 shows a significant upfield shift (0.764 ppm) and a broadening when compared with that of the free ligand. This is obviously contrary to the expected downfield shift due to the position next to an imine donor site. However, detailed analysis of the solid structure of **2** reveals that the H_5 atom is shielded by a benzimidazole ring in front of it. Since the three benzimidazole rings are not really C_3-symmetrically arranged, one $C-H_5$ bond points nearly perpendicular to the frontal benzimidazole ring while the remaining two are mutually parallel with the H_5 atoms under the ring current. The

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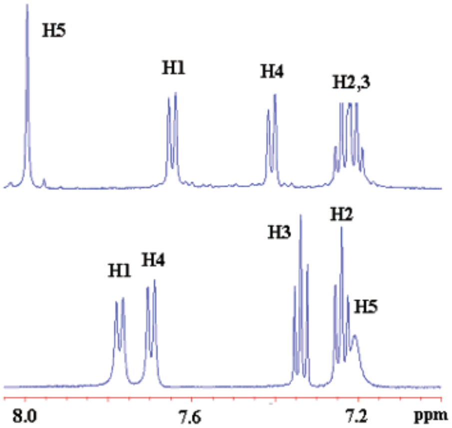

Figure 5. Sections of the ^{1}H NMR spectra of nteb (top) and complex **2** (bottom).

structure of **1** shows a similar situation for the H_5 atoms; obviously, the H_5 atoms will always be under aromatic shielding, regardless of a clockwise or anticlockwise propeller arrangement. Such a configuration justifies the large upfield shift of the H_5 signal in solution and may indicate that the propeller topology is maintained in solution, the slight broadening of the signal probably related to the fact that the three H_5 atoms are slightly inequivalent. However, the propeller conformation is labile owing to a facile twisting in solution; rapid chemical exchange between different conformations or dissociating intermediates seems to occur on the NMR time scale at room temperature in DMSO-d_6 solution.[15] Therefore, the ethylene linker shows no diastereotopic proton signals (averaging) although as many as 12 resonances may be theoretically expected for such a system providing they can be well resolved. On the other hand, the electrospray mass spectrum of complex **1** in acetonitrile displays a series of peaks corresponding to $[Mn(nteb)_2(ClO_4)]^+$ (*m/z* 1053), $[Mn(nteb)(ClO_4)]^+$ (*m/z* 603), and $[L + H]^+$ (*m/z* 450), confirming the existence of different species which may rapidly interconvert.

TGA Analyses. Thermogravimetric analysis of **1** displays two small weight loss events in the ranges 56−71 °C (ca. 3.22%) and 142−168 °C (ca. 2.73%), probably due to the release of one methanol molecule and the two water molecules, respectively. This finding is consistent with the structural analysis, which shows that the methanol molecule is loosely located between layers while the water molecules are involved in coordination. A massive weight loss was observed between 256 and 580 °C, corresponding to the decomposition of the compound. For compound **2** the first weight loss occurred between 79 and 121 °C, indicative of the removal of two water molecules (calculated 2.61%, observed 2.44%).

Conclusions

Two achiral tripodal tris(1-benzimidazolylethyl)amine ligands can adopt a propeller conformation to coordinate to one metal ion, leading to a double-propeller molecule whose chirality is determined by the mutual propeller orientation of the two ligands. The examples are the chiral $[Mn(nteb)_2(H_2O)_2]^{2+}$ cation in which two ligands adopt a homochiral conformation and the achiral $[Ag_2(nteb)_2]^{2+}$ cation in which the two ligands adopt a heterochiral conformation. The former is chiral individually but crystallizes as a racemate, while the later is actually a mesocate, a common phenomenon found for dinuclear triple-stranded helicates.[5,10] The propeller appearance of the two ligands is related to the coordination modes of the metal ions, indicating a way to control the stereochemistry of such systems. Spectroscopic investigation suggests that the solid-state structure might be predominant in the solution, although fast chemical exchange or rearrangements at room temperature prevent further insight into the stereochemistry. In addition, since the imine nitrogen atoms can act both as metal coordination donors and as hydrogen bond acceptors, there may be various choices of connectors between two ligands to form such double-propeller molecules, their stereochemistry being profoundly influenced by the connectors just as that of dinuclear triple-stranded helicates.

Experimental Section

Materials and General Methods. Tris(2-chloroethyl)amine[16] was prepared following the literature method. All other materials were purchased from commercial resources. Elemental analyses for C, H, and N were carried out with a Perkin-Elmer 240C elemental analyzer. ^{1}H NMR spectra were measured on a Varian ^{Unity}INOVA 500NB instrument using DMSO-d_6 as solvent and TMS as internal standard at room temperature. Infrared spectra were recorded from 4000 to 400 cm^{-1} on a Bruker EQINOX 55 FT-IR spectrometer. EPR spectra were measured in the X band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and an HP 5350B microwave counter. ES-MS was performed on a Quattro triple-quadrupole mass spectrometer with a mass to charge (*m*/*z*) range of 1400 using a standard electrospray ion source. FAB-MS spectra were obtained from a VG ZAB-HS spectrometer. Thermogravimetric analyses were carried out on a Perkin-Elmer TGA-7 analyzer.

Preparation of Tris(1-benzimidazolylethyl)amine (nteb). To a solution of 1*H*-benzimidazole (10 mmol) in 40 mL of dry THF/DMSO (10:1 v/v) under nitrogen was added dropwise a solution of freshly prepared *n*-butyllithium (10 mmol) in 20 mL of Et_2O with vigorous stirring at 0 °C. After 1/2 h a solution of tris(2-chloroethyl)amine (3.3 mmol) in 20 mL of THF was added over a period of 1 h. The reaction mixture was stirred continuously overnight at room temperature. A 50 mL portion of water was added to give a precipitant that was recrystallized in EtOH, giving a product with the composition $nteb{\cdot}2H_2O$. Yield: 84%. Anal. Calcd for $C_{27}H_{31}N_7O_2$: C, 66.58; H, 6.45; N, 20.04. Found: C, 66.67; H, 6.38; N, 20.16. FAB-MS (*m*/*z*): 450 (M^{+}+1), 449 (M^{+}). ^{1}H NMR (DMSO-d_6): δ 7.974 (s, 3H, H_5), 7.626 (d, 3H, H_1), 7.387 (d, 3H, H_4), 7.220 (m, 3H, H_3), 7.183 (m, 3H, H_2), 4.008 (t, 6H, H_6), 2.911 (t, 6H, H_7). IR (KBr, cm^{-1}): 3490b, 3050w, 2939w, 2829w, 1612w, 1498s, 1459m, 1366m, 747s.

Preparation of $[Mn(nteb)_2(H_2O)_2](ClO_4)_2{\cdot}CH_3OH$ (1). To a MeCN−MeOH solution (10 mL) of $Mn(ClO_4)_2{\cdot}6H_2O$ (0.362 g, 1 mmol) was added an ethanol solution (10 mL) of nteb (0.449 g,

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[15] (a) Su, C.-Y.; Cai, Y.-P.; Chen, C.-L.; Lissner, F.; Kang, B.-S.; Kaim, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 3371. (b) Fujita, M.; Nagao, S.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 1649.

[16] Marvel, C. S.; Pacevitz, H. A. *J. Am. Chem. Soc.* **1938**, *60*, 2816.

Table 1. Crystal Data and Structure Refinement

	1	2
empirical formula	$C_{55}H_{62}Cl_2MnN_{14}O_{11}$	$C_{58}H_{58}Ag_2F_6N_{14}O_6$
fw	1221.03	1376.92
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.471(4)	9.3390(12)
b (Å)	16.884(7)	10.2168(13)
c (Å)	19.906(8)	16.382(2)
α (deg)	77.930(7)	75.721(3)
β (deg)	88.063(7)	87.857(3)
γ (deg)	89.706(7)	71.738(3)
V (Å^3)	3111(2)	1437.2(3)
Z	2	1
ρ_{calcd} (g·cm^{-3})	1.304	1.591
μ (mm^{-1})	0.365	0.766
cryst size (mm)	0.26 × 0.20 × 0.18	0.30 × 0.26 × 0.18
no. of unique reflns	12445	6546
no. of obsd reflns	6892	3866
GOF on F^2	1.012	0.823
R^a [$I > 2\sigma(I)$]	0.0828	0.0516
$R_w{}^b$ [$I > 2\sigma(I)$]	0.2482	0.1279

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

Compound **1**			
Mn(1)−O(1)	2.1635(18)	Mn(1)−O(2)	2.2078(17)
Mn(1)−N(3)	2.261(2)	Mn(1)−N(14)	2.288(2)
Mn(1)−N(5)	2.313(2)	Mn(1)−N(12)	2.323(2)
O(1)−Mn(1)−O(2)	173.77(7)	O(1)−Mn(1)−N(3)	93.59(7)
O(2)−Mn(1)−N(3)	91.56(7)	O(1)−Mn(1)−N(14)	92.94(7)
O(2)−Mn(1)−N(14)	82.07(6)	N(3)−Mn(1)−N(14)	173.07(7)
O(1)−Mn(1)−N(5)	88.63(7)	O(2)−Mn(1)−N(5)	88.09(7)
N(3)−Mn(1)−N(5)	87.60(8)	N(14)−Mn(1)−N(5)	94.87(8)
O(1)−Mn(1)−N(12)	93.87(7)	O(2)−Mn(1)−N(12)	89.41(7)
N(3)−Mn(1)−N(12)	92.32(8)	N(14)−Mn(1)−N(12)	84.92(7)
N(5)−Mn(1)−N(12)	177.49(7)		
Compound **2**			
Ag(1)−N(4)	2.138(3)	Ag(1)−N(6)	2.184(4)
Ag(1)−N(2)	2.416(4)		
N(4)−Ag(1)−N(6)	152.09(15)	N(4)−Ag(1)−N(2)	115.31(14)
N(6)−Ag(1)−N(2)	91.65(14)		

1.0 mmol) with stirring at 50 °C for 45 min. The resulting mixture was filtered and left standing at room temperature to give colorless crystals. Yield: 64%. Anal. Calcd for $C_{55}H_{62}Cl_2MnN_{14}O_{11}$ (**1**): C, 54.05; H, 5.08; N, 16.05. Found: C, 53.87; H, 5.24; N, 15.82. IR (KBr, cm^{-1}): 3609m, 3457b, 3061w, 2935w, 2834w, 1613w, 1504s, 1462m, 1382m, 1094s, 749s, 624m.

Caution! Perchlorate salt is potentially explosive and should only be handled in small quantities, although we worked with it without any incident.

Preparation of [Ag_2(nteb)$_2$](CF_3CO_2)$_2$·2H_2O (2). The process was the same as that used for **1** but using $AgCF_3CO_2$ (0.221 g, 1 mmol) as the starting material. Yield: 82%. Anal. Calcd for $C_{58}H_{58}Ag_2F_6N_{14}O_6$ (**2**): C, 50.54; H, 4.21; N, 14.23. Found: C, 50.58; H, 4.19; N, 14.46%. ^{1}H NMR (DMSO-d_6) of 2: δ 7.774 (d, 3H, H_1), 7.698 (d, 3H, H_4), 7.338 (m, 3H, H_3), 7.241 (m, 3H, H_2), 7.210 (s, 3H, H_5), 4.192 (t, 6H, H_6), 3.073 (t, 6H, H_7). IR (KBr, cm^{-1}): 3466b, 3056w, 2966w, 2832w, 1687s, 1615w, 1504s, 1461m, 1378m, 744s.

X-ray Crystallographic Studies. The diffraction intensities of complexes **1** and **2** were collected (hemisphere technique) on a Bruker SMART 1 K diffractometer with a CCD area detector. Absorption corrections were performed using the SADABS program.[17] The structure was solved by direct methods and refined by full-matrix least-squares against F^2 of all data using SHELXTL software.[18] Anisotropical thermal factors were assigned to most of the non-hydrogen atoms with the exception of those of the perchlorate anions and the methanol molecule in **1** and fluorine atoms in **2**. The hydrogen atoms were included in the calculations isotropically but not refined. The perchlorate anions in **1** are disordered over two positions and were refined with fractional occupancy. The disordered CF_3 group of the $CF_3CO_2{}^-$ anion in **2** was refined with half-occupancy. A summary of parameters for the data collections and refinements is given in Table 1. Selected bond distances and bond angles are listed in Table 2

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Supporting Information Available: X-ray crystallographic file, in CIF format, for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Sheldrick, G. M. *SADABS. Program for scaling and correction of area detector data*; University of Göttingen: Göttingen, Germany, 1996.

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