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Trinuclear C_3-Symmetric Extension of Jacobsen's Catalyst: Synthesis, Characterization, and Catalytic Properties of a Chiral Trinuclear Mn^{III} Triplesalen Complex

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The synthesis of a chiral version of a triplesalen ligand has been performed in two steps starting from 2,4,6-triacetyl-1,3,5-trihydroxybenzene (**1**). Reaction with excess *trans*-(1R,2R)-1,2-cyclohexanediamine and *trans*-(1S,2S)-1,2-cyclohexanediamine provided the chiral triplesalen half units 2,4,6-tris[1-((1R,2R)-2-aminocyclohexylimino)ethyl]-1,3,5-trihydroxybenzene ($\mathbf{2^{RR}}$) and 2,4,6-tris[1-((1S,2S)-2-aminocyclohexylimino)ethyl]-1,3,5-trihydroxybenzene ($\mathbf{2^{SS}}$), respectively. The two enantiomeric pure triplesalen ligands H_6chand^{RR} and H_6chand^{SS} were obtained by reaction of the triplesalen half units with 3,5-di-*tert*-butylsalicylaldehyde. Reaction with $MnCl_2 \cdot 2H_2O$ under basic aerobic conditions afforded the chiral trinuclear triplesalen complexes $\mathbf{3^{RR}}$ and $\mathbf{3^{SS}}$. Single-crystal X-ray diffraction studies on both enantiomers showed the presence of the two ionization isomers $[(chand)\{Mn^{III}Cl(MeOH)\}_3]$ and $[(chand)\{Mn^{III}(MeOH)_2\}_3]Cl_3$ in the solid state, resulting in the formulation of **3** (either $\mathbf{3^{RR}}$ or $\mathbf{3^{SS}}$) as $[(chand)\{Mn^{III}Cl(MeOH)\}_3][(chand)\{Mn^{III}(MeOH)_2\}_3]Cl_3$. The crystal structures exhibit chiral hydrophobic channels of ~8 Å diameter decorated with *tert*-butyl groups. These form left-handed helices in the $\mathbf{3^{RR}}$ enantiomer and right-handed helices in the $\mathbf{3^{SS}}$ enantiomer. Magnetic measurements are in accord with weak exchange interactions between the Mn^{III} $S_i = 2$ ions and strong local magnetic anisotropy as has been found in other trinuclear Mn^{III}_3 triplesalen complexes. As a proof-of principal, we have investigated the catalytic ability of the two enantiomers in the enantioselective epoxidation of unfunctionalized olefins. The chiral trinuclear Mn^{III}_3 triplesalen acts under non-optimized conditions as a catalyst with relatively good yields and moderate enantiomeric excess.

Introduction

In 1990, Jacobsen et al.[1] and Katsuki et al.[2] independently reported chiral Mn^{III} salen Schiff base complexes as catalysts for the asymmetric epoxidation of unfunctionalized *cis*-olefins. Since then, the development of chiral Schiff base ligands and their corresponding metal complexes has received great interest,[3−9] as optically active epoxides have been used as chiral building blocks in organic synthesis for various regio- and stereoselective ring-opening reactions.[10] While the details of the mechanism for the asymmetric epoxidation of olefins is still a matter of debate, it is postulated that the reaction proceed via two successive steps (Scheme 1).[11] In the first step, a Mn^{III} center reacts with the external oxidant, like PhIO, H_2O_2, NaOCl, and etc., to yield a high-valent Mn^{V}=O species. While this Mn^{V}=O species may further react with 1 equiv of a Mn^{III} unit providing a Mn^{IV}−O−Mn^{IV} species, the monomeric Mn^{V}=O species is generally considered to be the active species. In the second step, the stereochemistry-determining step, the oxygen atom of the Mn^{V}=O unit is transferred to the olefinic double bond. A folded geometry of the salen ligand accompanied by the formation of a chiral pocket has been argued to be an essential element for the enantioselectivity of the epoxidation.[12−20]

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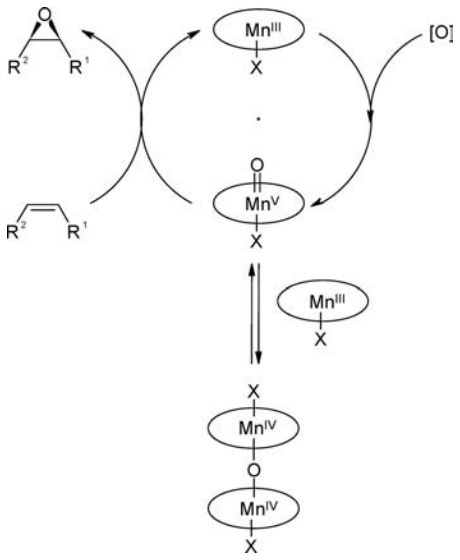
Scheme 1. Proposed Mechanisms for the Enantioselective Epoxidation of Unfunctionalized Olefins by Chiral Mn^{III} Salen Catalysts[11]



Despite this epoxidation reactivity, salen complexes with various metal ions have been identified as effective catalysts in a wide range of transformations like the enantioselective cyclopropanation of styrenes, asymmetric aziridination of olefins, enantioselective ring-opening of epoxides, Diels–Alder cycloaddition, etc.[21−25] For the asymmetric nucleophilic ring-opening of epoxides by chromium salen complexes, a mechanism was established involving catalytic activation of both the nucleophile and the electrophile in a bimetallic rate-determining step.[26−28] By using covalently linked dinuclear salen complexes, not only the intramolecular pathway but also an intermolecular pathway was enhanced. This observation "indicates that dimer reacts more rapidly with dimer, than does monomer with monomer" and "suggests that the design of covalently linked systems bearing three or more metal salen units may be worth-while".[29]

In our ongoing efforts for a rational development of new single-molecule magnets (SMMs), that is, molecules that can be magnetized without the necessity of cooperative effects, we have designed the parent ligand triplesalen (Scheme 2).[30,31] This ligand combines the phloroglucinol (1,3,5-trihydroxybenzene) bridging unit for high-spin ground states by ferromagnetic interactions[32−36] through the spin-polarization mechanism[37−41] with a salen-like coordination environment for a strong magnetic anisotropy.[42−44] Using trinuclear triplesalen complexes as molecular building blocks in combination with hexacyanometallates, we have been able to synthesize a new class of heptanuclear complexes comprised of two trinuclear triplesalen building blocks bridged by the hexacyanometallate,[45,46] where the heptanuclear complex $\mathbf{Mn^{III}_6Cr^{III}}$ behaves as a SMM.[45]

Herein, we describe the synthesis of the chiral triplesalen ligand H_6chand, which we envision as the C_3-symmetric trinuclear extension of the Jacobsen ligand H_2salen′ (H_2salen′ = (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine)[47] and its trinuclear Mn^{III} complex. Our motivation for this project is two-fold. First, the study of trinuclear complexes of the ligand chand^{6-} in enantioselective catalysis should enlighten cooperative effects,[48] as proposed by Jacobsen.[29] As the trinuclear triplesalen complexes exhibit bowl-shaped molecular structures, we want to examine the efficiency of a chiral pocket formed by a mononuclear salen complex compared to that of a chiral bowl formed by a trinuclear triplesalen complex.[31] On the other hand, the combination of chirality and single-molecule magnetism promises access to multifunctional molecular materials.[49−53] Furthermore, our heptanuclear SMMs (vide supra) possess an

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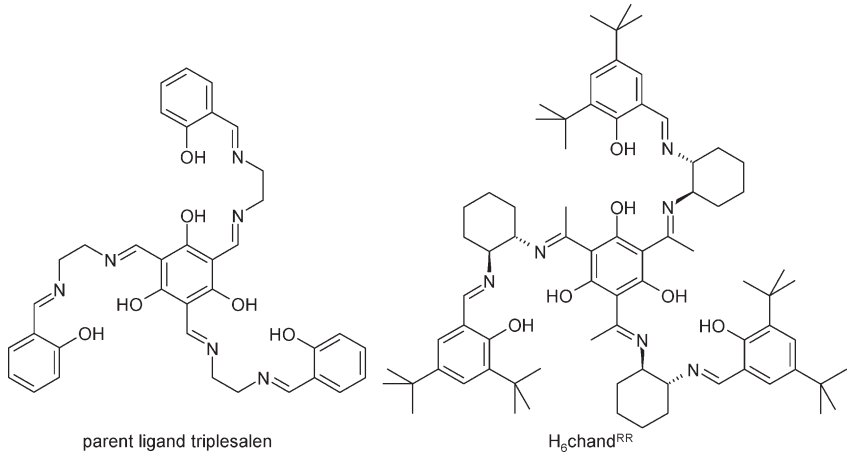
Scheme 2



inversion center. Thus, the two triplesalen building blocks are of opposing chirality. The use of enantiomerically pure trinuclear triplesalen building blocks would offer new synthetic opportunities for access to tetranuclear M_3M' units and heterotrimetallic $M_3M'M''_3$ units. As a first application, we report on the enantioselective epoxidation catalyzed by the chiral Mn^{III} triplesalen complex.

Experimental Section

Materials. All reagents were obtained from commercial sources and used as supplied, unless otherwise noted. 2,4,6-Triacetyl-1,3,5-trihydroxybenzene (**1**) was prepared according to the reported procedure.[54] Enantiomerically pure *trans*-(1R,2R)-1,2-cyclohexanediamine and *trans*-(1S,2S)-1,2-cyclohexanediamine were obtained by an established kinetic resolution.[55] The purity of *cis*-stilbene, *trans*-stilbene, 1,2-dihydronaphthalene, 1-phenylcyclohexene, *cis*-*β*-methylstyrene, *trans*-*β*-methylstyrene, and 1-decene was checked using ^{1}H NMR spectroscopy and gas chromatography (GC). Iodosylbenzene was prepared by the hydrolysis of iodobenzene diacetate and was kept in the dark with a coating of aluminum foil.

2,4,6-Tris[1-((1R,2R)-2-aminocyclohexylimino)ethyl]-1,3,5-trihydroxybenzene, 2^{RR}. 2,4,6-Triacetyl-1,3,5-trihydroxybenzene (**1**; 0.50 g, 2.0 mmol) was added to a solution of *trans*-(1R,2R)-1,2-cyclohexanediamine (2.0 g, 17.54 mmol) in EtOH (20 mL) and stirred at room temperature for 6 days, during which the color of the solution changed to deep red. The solution was filtered and evaporated under a vacuum at 50 °C to yield a red oil. Diethylether (100 mL) was added to the red oil and stirred for 1 h. The suspension was filtered to remove a light yellow solid, and the filtrate was evaporated under a vacuum at 50 °C to yield again a red oil. This oil was dissolved in water (30 mL) and extracted with CH_2Cl_2 (100 mL). The CH_2Cl_2 solution was further washed with water (2 × 25 mL) and dried over Na_2SO_4. Upon evaporation of the CH_2Cl_2, a sticky yellow oil was obtained. Yield: 0.57 g (53%). IR (KBr): $\tilde{\nu}$/cm^{-1} 3418m, 3374m, 3290m, 2928s, 2859s, 1531s, 1456m, 1421m, 1371m, 1338m, 1319m. ^{1}H NMR (500.15 MHz, $CDCl_3$): δ 1.17−1.37 (m, 12H), 1.44 (s, br, 6H), 1.73−1.76 (m, 6H), 1.90−1.96 (m, 6H), 2.57 (s, 9H), 2.71−2.86 (m, 3H), 3.22−3.32 (m, 3H), 13.11−14.39 and 18.53 (s, br, 3H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 18.7, 24.6, 24.9, 32.9, 34.2, 55.1, 60.1, 105.7, 170.0, 185.7. MS-ESI (+ve, CH_2Cl_2): m/z 541.3 $[M + H]^+$. $[\alpha]^{20}_D$ = −161.0 (±5.0), C = 2.01, $CHCl_3$. Anal. Calcd for $C_{30}H_{48}N_6O_3 \cdot 0.4CH_2Cl_2$: C, 63.53; H, 8.56; N, 14.62. Found: C, 63.60; H, 8.72; N, 14.44.

2,4,6-Tris[1-((1S,2S)-2-aminocyclohexylimino)ethyl]-1,3,5-trihydroxybenzene, 2^{SS}. The same synthetic procedure has been used as applied for the synthesis of half unit 2^{RR} despite using *trans*-(1S,2S)-1,2-cyclohexanediamine. Yield: 0.66 g (61%). IR (KBr): $\tilde{\nu}$/cm^{-1} 3418m, 3366m, 3281m, 2930s, 2857s, 1533s, 1458m, 1421m, 1373m, 1340m, 1321m. ^{1}H NMR (500.15 MHz, $CDCl_3$): δ 1.18−1.40 (m, 12H), 1.63 (s, br, 6H), 1.72−1.74 (m, 6H), 1.90−1.97 (m, 6H), 2.57 (s, 9H), 2.78−2.86 (m, 3H), 3.25−3.33 (m, 3H), 13.11−14.27 (s, br, 3H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 18.4, 24.5, 24.8, 32.7, 34.1, 55.0, 60.0, 105.0, 170.4, 185.6. MS-ESI (+ve, CH_2Cl_2): m/z 541.3 $[M + H]^+$. $[\alpha]^{20}_D$ = +156.0 (±5.0), C = 2.00, $CHCl_3$. Anal. Calcd for $C_{30}H_{48}N_6O_3 \cdot 0.5CH_2Cl_2$: C, 62.81; H, 8.47; N, 14.41. Found: C, 62.62; H, 8.63; N, 14.20.

2,4,6-Tris{1-[(1R,2R)-2-(3,5-di-*tert*-butylsalicylaldimino)cyclohexylimino]ethyl}-1,3,5-trihydroxybenzene, H_6chand^{RR}. Half-unit 2^{RR} (0.54 g, 1.0 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (0.70 g, 3.0 mmol) were stirred in MeOH (15 mL) for 20 h, during which a yellow precipitate formed, which was isolated by filtration, washed with methanol, and dried under air. Yield: 0.71 g (60%). IR (KBr): $\tilde{\nu}$/cm^{-1} 3418w, 2951−2862m, 1628s, 1591m, 1530s, 1456s, 1441s, 1361m, 1252m. ^{1}H NMR (500.15 MHz, $CDCl_3$): δ 1.23−1.25 (m, 27H), 1.40 (s, 27H), 1.45−2.17 (m, 24H), 2.23−2.44 (m, 9H), 3.10−3.30 (m, 3H), 3.70−3.88(m, 3H), 6.95−6.97 (m, 3H), 7.31−7.34 (m, 3H), 8.27−8.37 (m, 3H), 13.67−14.47 and 18.26 (m, 3H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 18.0, 18.5, 18.7, 23.4, 23.8, 24.2, 29.5, 31.5, 32.1, 32.7, 34.0, 35.0, 56.0, 56.3, 71.9, 72.5, 105.7, 117.7, 126.1, 127.0, 136.4, 139.9, 158.0, 166.2, 169.6, 170.2, 185.4. MS-ESI (+ve, CH_2Cl_2): m/z 1190.8 $[M + H]^+$. $[\alpha]^{20}_D$ = −805.0 (±5.0), C = 2.12, $CHCl_3$. Anal. Calcd for $C_{75}H_{108}N_6O_6 \cdot 0.5H_2O$: C, 75.15; H, 9.16; N, 7.00. Found: C, 75.30; H, 9.26; N, 6.85.

2,4,6-Tris{1-[(1S,2S)-2-(3,5-di-*tert*-butylsalicylaldimino)cyclohexylimino]ethyl}-1,3,5-trihydroxybenzene, H_6chand^{SS}. The same synthetic procedure has been used as applied for the synthesis of the ligand H_6chand^{RR} despite using half-unit 2^{SS}. Yield: 0.80 g (67%). IR (KBr): $\tilde{\nu}$/cm^{-1} 3418w, 2953−2862m, 1628s, 1587m, 1530s, 1456s, 1441s, 1361m, 1252m. ^{1}H NMR (500.15 MHz, $CDCl_3$): δ 1.21−1.27 (m, 27H), 1.40−1.42 (m, 27H), 1.42−2.17 (m, 24H), 2.35−2.48 (m, 9H), 3.15−3.29 (m, 3H), 3.70−3.86(m, 3H), 6.95−6.98 (m, 3H), 7.31−7.35 (m, 3H), 8.30−8.37 (m, 3H), 13.38−14.53 (m, 3H). ^{13}C NMR (125.77

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MHz, $CDCl_3$): δ 18.0, 18.4, 18.5, 18.8, 23.3, 23.6, 23.7, 24.2, 29.5, 31.5, 32.1, 32.8, 34.1, 35.0, 56.3, 56.9, 71.9, 72.6, 105.2, 108.2, 117.8, 126.1, 127.0, 136.5, 140.0, 158.0, 166.3, 169.3, 169.6, 170.4, 185.4. MS-ESI (+ve, CH_2Cl_2): *m*/*z* 1190.8 $[M + H]^+$. $[\alpha]^{20}_D = +807.0$ (±5.0), $C = 2.01$, $CHCl_3$. Anal. Calcd for $C_{75}H_{108}N_6O_6 \cdot 0.5H_2O$: C, 75.15; H, 9.16; N, 7.00. Found: C, 75.11; H, 9.04; N, 7.05.

Preparation of [(chand^{RR}){Mn^{III}Cl(MeOH)}$_3$][(chand^{RR})-{Mn^{III}(MeOH)$_2$}$_3$]Cl$_3$, 3^{RR}. $MnCl_2 \cdot 2H_2O$ (0.26 g, 1.6 mmol) and Et_3N (0.3 mL) were added to a solution of the ligand H_6chand^{RR} (0.595 g, 0.5 mmol) in methanol (20 mL). The resulting deep brown solution was stirred for 15 h. Slow diffusion of diethylether (100 mL) resulted in a deep-brown crystalline solid, which was isolated by filtration and dried under air. Yield: 0.56 g (68%). IR (KBr): $\tilde{\nu}/cm^{-1}$ 3435br, 2949−2858s, 1620s, 1535s, 1477s, 1250s. MS-ESI (+ve, CH_2Cl_2): *m*/*z* 1419.6 $[(chand^{RR})Mn^{III}{}_3Cl_2]^+$ and $\{[(chand^{RR})Mn^{III}{}_3Cl_2]\}_2^{2+}$, 691.30 $[(chand^{RR})Mn^{III}{}_3Cl]^{2+}$, 449.3 $[(chand^{RR})Mn^{III}{}_3]^{3+}$. $[\alpha]^{20}_D = -3781$ (±5.0), $C = 0.0164$, $CHCl_3$. Anal. Calcd for $(C_{159}H_{240}Cl_6Mn_6N_{12}O_{21} \cdot 6H_2O)$: C, 57.76%; H, 7.68%; N, 5.08%. Found. C, 57.50%; H, 7.30%; N, 5.26%.

Preparation of [(chand^{SS}){Mn^{III}Cl(MeOH)}$_3$][(chand^{SS}){Mn^{III}-(MeOH)$_2$}$_3$]Cl$_3$, 3^{SS}. The same synthetic procedure has been used as applied for the synthesis of complex **3**^{RR} but using the ligand H_6chand^{SS}. Yield: 0.51 g (63%). IR (KBr): $\tilde{\nu}/cm^{-1}$ 3441br, 2951−2864s, 1620s, 1537s, 1479s, 1252s. MS-ESI (+ve, CH_2Cl_2): *m*/*z* 2873.7 $[(chand^{SS})_2Mn^{III}{}_6Cl_5]^+$, 2146.4 $[(chand^{SS})_2Mn^{III}{}_6Cl_4]^{2+}$, 1419.6 $[(chand^{SS})Mn^{III}{}_3Cl_2]^+$ and $\{[(chand^{SS})Mn^{III}{}_3Cl_2]\}_2^{2+}$. $[\alpha]^{20}_D = +3787.0$ (±5.0), $C = 0.0170$, $CHCl_3$. Anal. Calcd for $(C_{159}H_{240}Cl_6Mn_6N_{12}O_{21} \cdot 3H_2O)$: C, 58.72%; H, 7.62%; N, 5.17%. Found: C, 58.37%; H, 7.44%; N, 5.37%.

General Procedure for Catalytic Reactions. Complex **3** (7.30 mg, 0.005 mmol) was dissolved in CH_2Cl_2 (2 mL). To this solution were added the alkene substrate (0.1 mmol) and iodosylbenzene (61.0 mg, 0. 277 mmol) and were stirred at room temperature for 15 h. The solvent was evaporated and the residue treated with CH_2Cl_2 (0.2 mL) and passed through a short SiO_2 column. The column was washed with CH_2Cl_2 (10 mL). The resulting solution was evaporated, and ^{1}H NMR spectra were recorded after dissolving the residue in $CDCl_3$ (0.6 mL). The conversion was calculated from the area of the olefine and epoxide signals obtained in the ^{1}H NMR spectrum using the formula: conversion = ([product])/([substrate] + [product]) × 100%. GC and GC-MS measurements were also performed to identify the products.

X-Ray Crystallography. Crystal data for **3**^{RR} · $3Et_2O \cdot 7.5CH_3OH$: $M = 3660.64$ g mol^{-1}, $C_{178.50}H_{300}Cl_6Mn_6N_{12}O_{31.50}$, hexagonal, space group $P6_3$, $a = 22.4648(2)$ Å, $b = 22.4648(2)$ Å, $c = 24.2100(2)$ Å, $V = 10581.08(16)$ Å^3, $Z = 2$, $\rho = 1.149$ g cm^{-3}, $\mu = 0.486$ mm^{-1}, $F(000) = 3918$, crystal size = 0.30 × 0.30 × 0.18 mm^3. Crystals of **3**^{RR} · $3Et_2O \cdot 7.5CH_3OH$ were removed from the mother liquor and immediately cooled to 100(2) K on a Nonius KappaCCD diffractometer with Mo Kα radiation using a graphite monochromator. A total of 115 639 reflections ($2.91 < \Theta < 27.48°$) were collected, of which 13 830 reflections were unique (R(int) = 0.056). Data reduction and absorption correction were performed with DENZO and SCALEPACK.[56] The structure was solved with the program SHELXS-97[57,58] and refined using SHELXL-97[58] to $R = 0.0513$ for 12 920 reflections with $I > 2\sigma(I)$ and $R = 0.0561$ for all reflections; Max/min residual electron density were 0.910 and −0.629 e Å^{-3}, respectively.

Crystal data for Complex **3**^{SS} · $7.5CH_3OH$: $M = 3438.28$ g mol^{-1}, $C_{166.50}H_{270}Cl_6Mn_6N_{12}O_{28.50}$, hexagonal, space group $P6_3$, $a = 22.5033(15)$ Å, $b = 22.5033(15)$ Å, $c = 24.384(2)$ Å, $V = 10693.7(14)$ Å^3, $Z = 2$, $\rho = 1.068$ g cm^{-3}, $\mu = 0.476$ mm^{-1}, $F(000) = 3666$, crystal size = 0.80 × 0.08 × 0.04 mm^3. Crystals of **3**^{SS} · $7.5CH_3OH$ were removed from the mother liquor and immediately cooled to 183(2) K on a Bruker AXS SMART diffractometer (three-circle goniometer with 1K CCD detector, Mo Kα radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435, and 230 frames ($\varphi = 0$, 88, and 180°) at a detector distance of 5 cm). A total of 53 910 reflections ($1.34 < \Theta < 24.99°$) were collected, of which 12 514 reflections were unique (R(int) = 0.0965). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.03.[59] The structure was solved with the program SHELXS-97[57,58] and refined using SHELXL-97[58] to $R = 0.0693$ for 9072 reflections with $I > 2\sigma(I)$ and $R = 0.1048$ for all reflections; Max/min residual electron density were 1.031 and −0.491 e Å^{-3}, respectively.

Other Physical Measurements. FTIR spectra were recorded on a Shimadzu FTIR 8300 spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX500 using the solvent as an internal standard. Mass spectra were obtained on a Bruker Esquire 3000 mass spectrometer. Elemental analyses were carried out in the Microanalysis Laboratory, Bielefeld University. GC analyses were performed on a Shimadzu GC2010 and GC-MS analysis on a Shimadzu QP2010S.

Results and Discussion

Synthesis and Characterization. Symmetrical salen ligands are very common and can easily be prepared by one-pot condensation of one diamine with two identical aldehyde or ketone derivatives. The controlled synthesis of unsymmetrical salen ligands (not a mixture of symmetrical and unsymmetrical compounds) containing two different aldehyde or ketone derivatives is not trivial because the simple condensation methodology used for the synthesis of symmetrical salen ligands is no longer applicable. Therefore, a stepwise protocol that requires a salen *half unit* is necessary,[60−64] and this intermediate would provide the opportunity for the synthesis of the desired unsymmetrical salen ligand by the reaction of the remaining amine with the other aldehyde or ketone derivative. However, a salen half unit is not always accessible[61] and mainly requires a differentiation of the reactivity of the two amine functions.[65] We have shown that, for a stepwise procedure, the generation of a more stable ketimine half unit and subsequent reaction with an aldehyde is a promising sequence.[30,31]

In this respect, two principal reaction routes are feasible to synthesize the targeted chiral triplesalen ligand **A** (Scheme 3). Route A requires the synthesis of the chiral triplesalen ketimine half unit **B** ($R^2 = CH_3$) in the first step, which reacts in the second step with salicylaldehyde **C** ($R^1 = H$). Route B requires the synthesis of the chiral salen ketimine half unit **D** ($R^1 = CH_3$), which reacts

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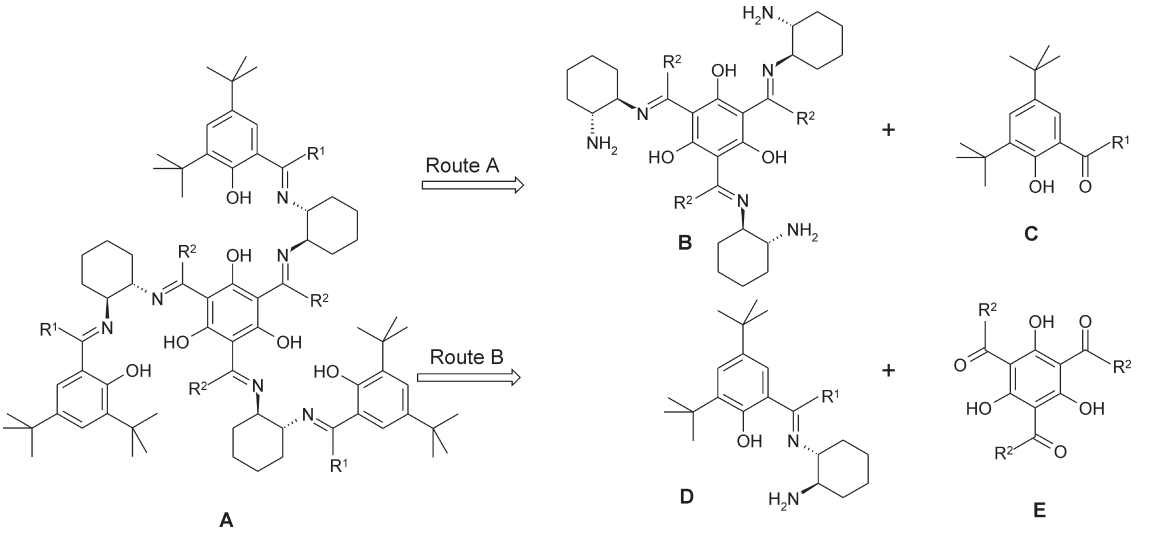
Scheme 3



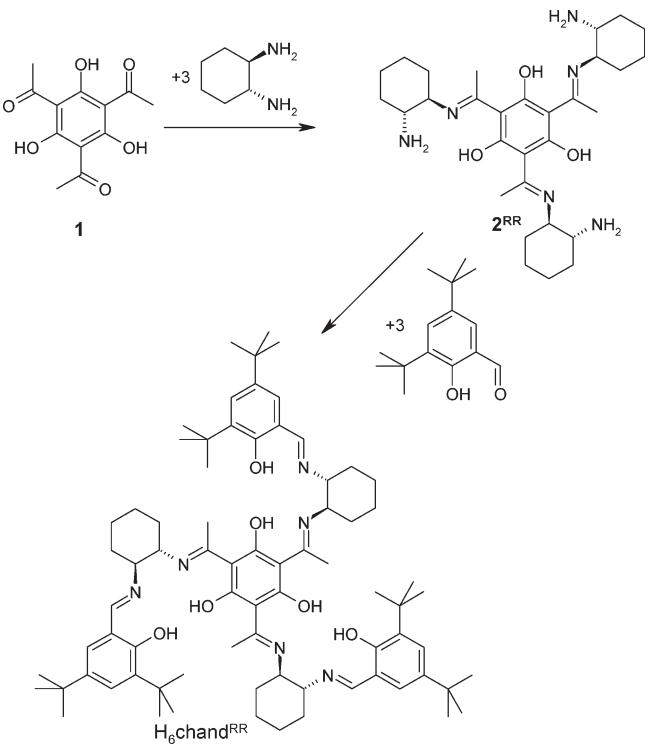
further with 2,4,6-triformyl-1,3,5-trihydroxybenzene **E** (R^2 = H). For the synthesis of the parent nonchiral triplesalen ligand, we have chosen route A.[30,31] The isolation of the triplesalen ketimine half unit was based on the differential reactivity of the diamine used, that is, 2-methyl-1,2-diaminopropane, which does not react with the sterically more crowded amine function with ketones.[65]

Although, the use of 1,2-cyclohexanediamine gives no opportunity to rely on differential reactivity of the diamine, salen half units with this diamine have already been reported.[62−64] Therefore, we have tried to follow route A by reacting triketone **1** with *trans*-(R,R)-1,2-cyclohexanediamine (Scheme 4). After several optimization steps, we have been able to obtain a feasible protocol for the synthesis of the chiral triplesalen half unit $\mathbf{2}^{RR}$. Further reaction with 3 equiv of 3,5-di-*tert*-butylsalicylaldehyde produces the enantiomerically pure ligand H_6chand^{RR}. The above synthetic strategy has been applied to prepare both enantiomers H_6chand^{RR} and H_6chand^{SS}. Reaction of the individual ligand with $MnCl_2 \cdot 2H_2O$ in methanol under basic aerobic conditions followed by diffusion of diethyl ether afforded the enantiomerically pure complexes $\mathbf{3}^{RR}$ and $\mathbf{3}^{SS}$ as deep brown crystals.

The infrared spectra of the chiral triplesalen half units **2** formed by the condensation of **1** (Scheme 4) with *trans*-(1R,2R)-1,2-cyclohexanediamine or *trans*-(1S,2S)-1,2-cyclohexanediamine are almost identical and show a strong band at around 1532 cm^{-1} due to the ν(C=N) vibration of the ketimine units. In the infrared spectra of the ligands H_6chand^{RR} and H_6chand^{SS} a new band at 1628 cm^{-1} due to the ν(C=N) vibration of the aldimine units formed, and a strong band at 1589 cm^{-1} due to ν(C=C) vibrations of the aromatic rings appears. The infrared spectra of complex $\mathbf{3}^{RR}$ and complex $\mathbf{3}^{SS}$ are identical. The ν(C=N) band of the aldimine units shifts from 1628 cm^{-1} in the ligand to 1620 cm^{-1} upon complexation, while the ketimine ν(C=N) vibration shifts only slightly from 1532 cm^{-1} to 1535 cm^{-1}. A strong band due to phenolic ν(C−O) vibrations appears at 1250 cm^{-1}.

^{1}H NMR spectra of the chiral triplesalen half units **2** show a singlet for the methyl groups at 2.57 ppm and a broad band for the amine protons at 1.44 ppm. Signals for

Scheme 4



the protons at the cyclohexane moieties appear as multiplets between 1.70 and 3.30 ppm. The ^{1}H NMR spectra of the ligands exhibit signals at 1.23−1.25 ppm and 1.40−1.42 ppm of the *tert*-butyl groups. However, the signals for ketimine, aldimine, and OH protons appear as complicated multiplets. This phenomenon has already been observed in the parent triplesalen ligand.[30] Temperature-dependent ^{1}H NMR spectra revealed a simplification of the spectra at higher temperatures, indicating a dynamic process on the timescale of the NMR experiment. This process might be assigned to cis/trans isomerization of the ketimine C=N bonds.[66,67] The signals of the protons

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Table 1. Selected Bond Lengths [Å] and Bond Angles [deg] of Complex $\mathbf{3}^{\mathbf{RR}}$

Mn1−N11	2.029(3)	O11−Mn1−N11	90.71(11)
Mn1−N12	1.972(3)	O12−Mn1−N12	91.14(11)
Mn1−O11	1.872(2)	O11−Mn1−N12	170.97(12)
Mn1−O12	1.886(3)	O12−Mn1−O11	92.94(11)
Mn1−Cl1	2.4636(10)	Cl1−Mn1−O41	175.93(8)
Mn1−O41	2.416(3)	N11−Mn1−N12	83.49(12)
Mn2−N21	2.025(3)	O21−Mn2−N22	172.38(12)
Mn2−N22	1.972(3)	O22−Mn2−N21	171.58(11)
Mn2−O21	1.891(2)	O21−Mn2−N21	91.70(11)
Mn2−O22	1.905(2)	O22−Mn2−N22	90.33(11)
Mn2−O42	2.195(3)	N21−Mn2−N22	82.17(12)
Mn2−O43	2.275(3)	O42−Mn2−O43	178.02(10)

attached to the cyclohexane ring appear as multiplets in the range 1.45−3.90 ppm.

The electrospray ionization (ESI; positive mode) mass spectra of the chiral triplesalen half units and the ligands show $[M + H]^+$ as a base peak (100%). The ESI (positive mode) mass spectrum of a CH_2Cl_2 solution of complex $\mathbf{3}^{\mathbf{RR}}$ shows a 100% peak at 1419.6 which corresponds to the composition $[(chand^{RR})Mn_3Cl_2]^+$. However, close inspection of the isotope distribution pattern indicates that this signal is a superposition of $[(chand^{RR})Mn_3Cl_2]^+$ and $\{[(chand^{RR})Mn_3Cl_2]_2\}^{2+}$ in an approximate 1:2 ratio. Moreover, peaks for $[(chand^{RR})Mn_3Cl]^{2+}$ and $[(chand^{RR})Mn_3]^{3+}$ appear at 691.3 and 449.3, respectively. The ESI (positive mode) mass spectrum of complex $\mathbf{3}^{\mathbf{SS}}$ shows a 100% peak at 2873.7 corresponding to $\{[(chand^{SS})Mn_3Cl_3][(chand^{SS})Mn_3Cl_2]\}^+$. A peak at 2146.4 (70%) corresponds to the composition of $[(chand^{SS})_3Mn_9Cl_7]^{2+}$, which may be formulated as $\{3[(chand^{SS})Mn_3Cl_3]\text{-}2Cl^-\}^{2+}$. Similar to complex $\mathbf{3}^{\mathbf{RR}}$, in the mass spectrum of complex $\mathbf{3}^{\mathbf{SS}}$, the peak at 1419.6 appears and shows a similar kind of isotope distribution pattern. Hence, the mass spectra indicate that complex **3** may form supramolecular aggregates in solution.

Molecular and Crystal Structures. Single crystals of the trinuclear Mn^{III} complexes were obtained for both enantiomers and were identified by single-crystal X-ray diffraction as $\mathbf{3}^{\mathbf{RR}}\cdot 3Et_2O\cdot 7.5CH_3OH$ and $\mathbf{3}^{\mathbf{SS}}\cdot 7.5CH_3OH$, crystallized in the hexagonal space group $P6_3$. The molecular structures of complex $\mathbf{3}^{\mathbf{RR}}$ and complex $\mathbf{3}^{\mathbf{SS}}$ are identical despite being enantiomers. Therefore, we only focus on $\mathbf{3}^{\mathbf{RR}}$. Selected bond lengths and angles for complex $\mathbf{3}^{\mathbf{RR}}$ are listed in Table 1.

Interestingly, the asymmetric unit of crystals of complex $\mathbf{3}^{\mathbf{RR}}\cdot 3Et_2O\cdot 7.5CH_3OH$ (Figure 1a) consists of two differently coordinated Mn ions, each forming a third of a trinuclear Mn triplesalen complex. Mn1 is coordinated by a salen-like ligand compartment of $(chand)^{6-}$, a chloride ion, and a methanol molecule, yielding a charge-neutral fragment. On the other hand, Mn2 is also coordinated by a salen-like ligand compartment but has no ligated chloride. Two coordinated methanol molecules result in a cationic fragment, and a noncoordinated chloride ion (Cl2) acts as a counteranion for charge neutrality. In the neutral fragment, the Mn^{III} ion is at a distance of 0.174 Å from the best N_2O_2 plane toward the chloride, while in the cationic fragment, the Mn^{III} ion is more in the plane (0.075 Å distance to the best N_2O_2 plane). The salen-ligand compartments with Mn−OPh bond lengths of

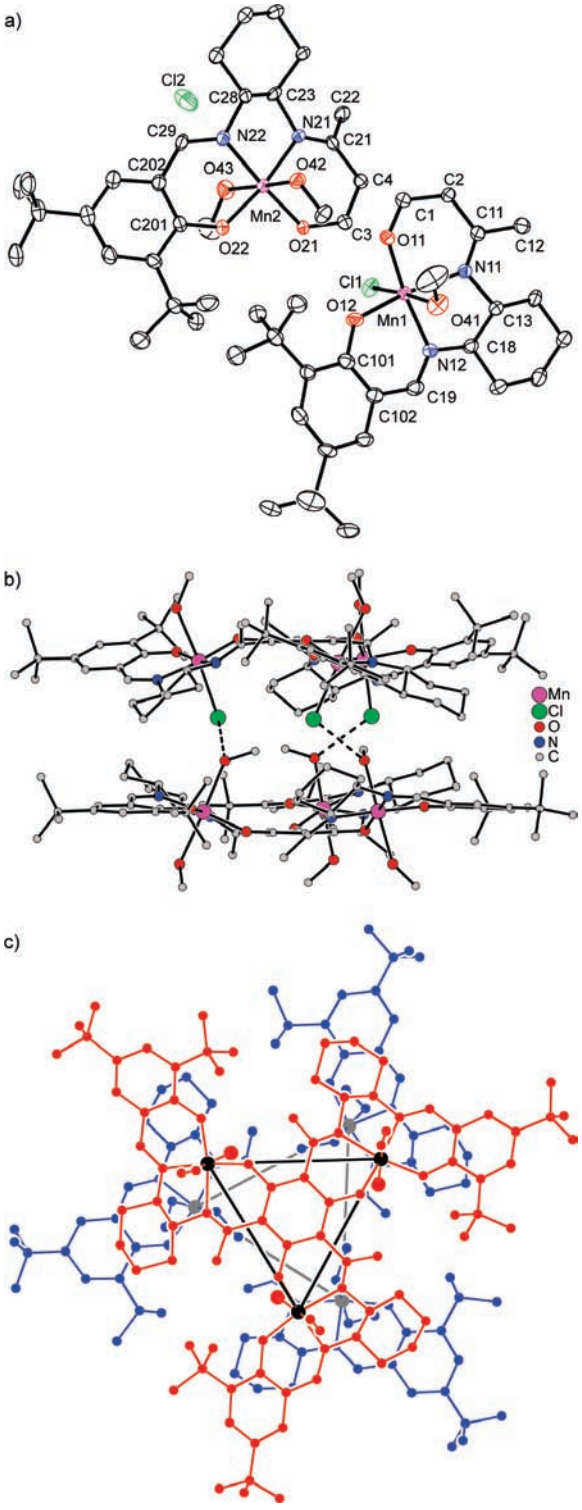

Figure 1. (a) Thermal ellipsoid plot of the asymmetric unit in crystals of $\mathbf{3}^{\mathbf{RR}}\cdot 3Et_2O\cdot 7.5CH_3OH$. Uncoordinated solvent molecules and hydrogen atoms have been omitted for clarity. (b) Molecular structures of the dimer of trimers unit in $\mathbf{3}^{\mathbf{RR}}$. (c) Top view of the "dimer of trimers" along the C_3 axis with two different skeletal colors. The Mn ions with ligated chlorides are drawn in black, and the other Mn ions are drawn in gray.

1.87−1.91 Å and Mn−N bond lengths of 1.97−2.03 Å are in accord with previously reported triplesalen Mn^{III} compounds.[45,68] The axial methanol molecules of the cationic fragment exhibit Mn−O bond distances of 2.20 Å and 2.28 Å. The trans influence of the chloride ion in the

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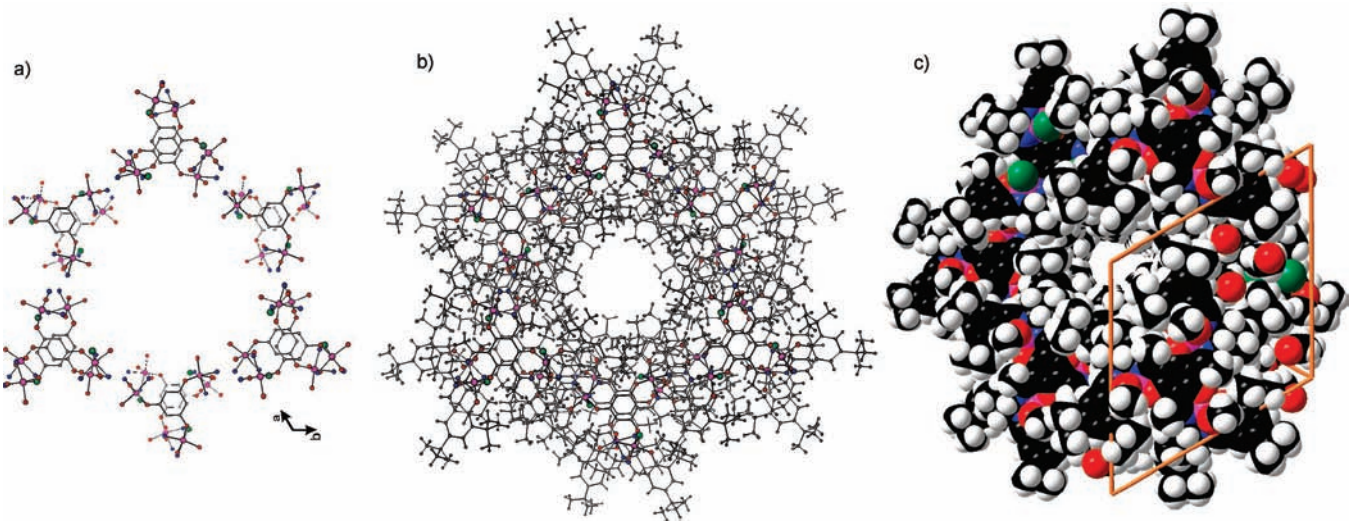


Figure 2. (a) Octahedron of "dimer of trimer" base unit generated by the 6_3 axis in $\mathbf{3}^{SS}$. Only the central phloroglucinol and the metal ions with their first coordination sphere are shown. The black bond molecules form a plane with the gray bonded molecules below this plane. (b) Same view and same molecules as in (a), but with all atoms shown. Note the central void decorated with *t*-butyl groups. (c) Space-filling model of $\mathbf{3}^{SS}$ over several units to visualize the hydrophobic channels.

neutral fragment results in a longer Mn−O distance of 2.42 Å.

A crystallographic C_3 axis generates the two triplesalen Mn^{III}_3 complexes: the neutral complex $[(chand^{RR})\{Mn^{III}Cl(MeOH)\}_3]$ and the tricationic complex $[(chand^{RR})\{Mn^{III}(MeOH)_2\}_3]^{3+}$ (Figure 1b).

The overall geometries of all trinuclear triplesalen complexes reported so far exhibit various degrees of ligand folding.[30,31,36,45,46,68] We identified the bent angles $\phi_{central}$ and $\phi_{terminal}$ as the best parameters for a quantitative estimation of ligand folding. The bent angle ϕ (introduced by Cavallo and Jacobsen)[17] is defined by $\phi = 180° - \angle M{-}X_{NO}{-}X_R$, where X_{NO} is the midpoint between adjacent N and O donor atoms and X_R is the midpoint of the six-membered chelate ring containing these N and O donor atoms. This bent angle is best suited to differentiate between a bending along an idealized line through neighboring N and O ligands and a line perpendicular to the former, resulting in a helical distortion.[31] The angles $\phi_{central}$ and $\phi_{terminal}$ are +14.1° and −8.8°, respectively, for the neutral Mn^{III}_3 molecule with ligated chlorides and +15.7° and −26.5°, respectively, for the tricationic Mn^{III}_3 molecule. The negative signs for $\phi_{terminal}$ illustrate bending toward the opposite site with $\phi_{central}$ as a reference. The trinuclear complexes of the ligand $H_6talen^{t\text{-}Bu_2}$ usually exhibit both bent angles as positive with a large value for $\phi_{central}$.[31,36] This leads to overall bowl-shaped geometries. A different sign obtained for the two molecules of **3** indicates an overall dish-like geometry, as may be seen in Figure 1b, and was observed in the trinuclear Mn^{III} complex of $H_6talen^{NO_2}$.[68]

The Mn···Mn distances are 7.07 Å and 7.09 Å for the neutral and the tricationic complexes, respectively. The closest Mn···Mn distance between the two molecules is 6.19 Å. The two molecules are not in a complete staggered comformation, but the two triangles formed by Mn1 ions and Mn2 ions, respectively, are rotated by 26.2° along the C_3 axis (Figure 1c) and are at a distance of 5.91 Å. Besides some weak C−H···Cl interactions, a driving force for the "dimer of trimer" formation may be the O−H···Cl hydrogen bonds with a distance of 3.01 Å formed by coordinated methanol molecules of the tricationic complex and the coordinated chloride ions of the neutral complex. The uncoordinated chloride ion is stabilized by O−H···Cl hydrogen bonds (d(O−Cl) = 3.02−3.13 Å) with two coordinated and two uncoordinated methanol molecules.

The crystal structures of the two isomers $\mathbf{3}^{RR}$ and $\mathbf{3}^{SS}$ exhibit chiral hydrophobic channels. Considering the "dimer of trimers" aggregates **3** as the base units, the 6_3 screw axis generates an "octahedron" of these units (Figure 2a). The central part of the octahedron is a void decorated only by the *t*-butyl groups (Figure 2b). The crystal structure of $\mathbf{3}^{SS}$ (and also $\mathbf{3}^{RR}$) exhibits there nearly empty channels along the 6_3 axis (Figure 2c). The diameter of these channels is ~8 Å based on atom-to-atom distances or ~6 Å considering the van der Waals radii. In $\mathbf{3}^{SS}$, the channels are only filled by groups of three methanol molecules having a distance of 12.5 Å to the next group of three methanol molecules. In $\mathbf{3}^{RR}$, these channels are filled by groups of ether molecules separated by 12.1 Å. We cannot rule out that more ill-defined solvent molecules may be present in those channels. The channels are chiral triple-helices, indicated in Figure 3 for $\mathbf{3}^{RR}$. The helices are left-handed for $\mathbf{3}^{RR}$ and right-handed for $\mathbf{3}^{SS}$.

Magnetic Susceptibility. Temperature-dependent magnetic susceptibility measurements of complex $\mathbf{3}^{RR}\cdot 6H_2O$ were performed on a microcrystalline sample in the temperature range of 2−290 K with an applied field of 1 T. As the individual magnetic properties of the tricationic complex $[(chand^{RR})\{Mn(MeOH)_2\}_3]^{3+}$ and of the neutral complex $[(chand^{RR})\{MnCl(MeOH)\}_3]$ cannot be separated by bulk magnetic measurements, we report the magnetic properties per average trinuclear Mn^{III} unit in $\mathbf{3}^{RR}\cdot 6H_2O$. The effective magnetic moment, μ_{eff}, is 8.35 μ_B at 290 K, which is close to the value of 8.49 for three noninteracting high-spin Mn^{III} ions (S_i = 2, g_i = 2.00). As the temperature is lowered from 290 to 100 K, μ_{eff} exhibits only a slight decrease from 8.35 μ_B to 8.10 μ_B

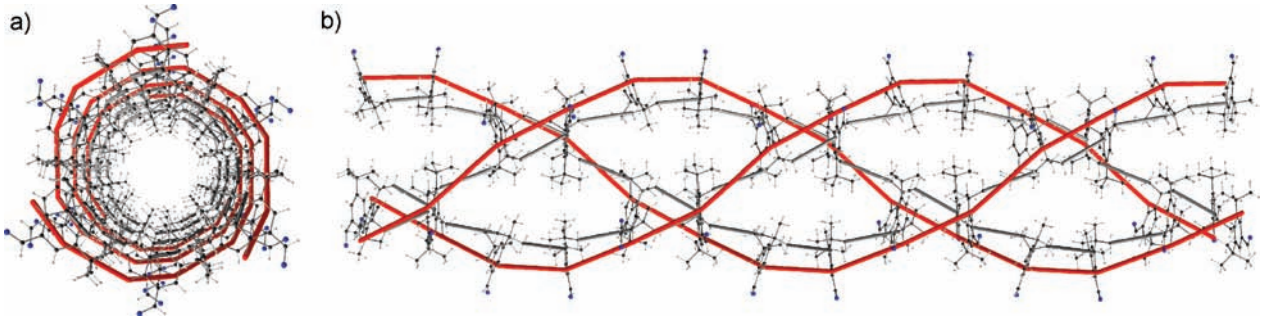


Figure 3. Visualization of the chiral triple-helical channels in $\mathbf{3^{RR}}$. The channels are displayed only with a part of the constituting molecules. The view in (a) is along the 6_3 axis and perpendicular to it in (b). The helicity is visualized by connecting the same phoroglucinol oxygen atom over three unit cells.

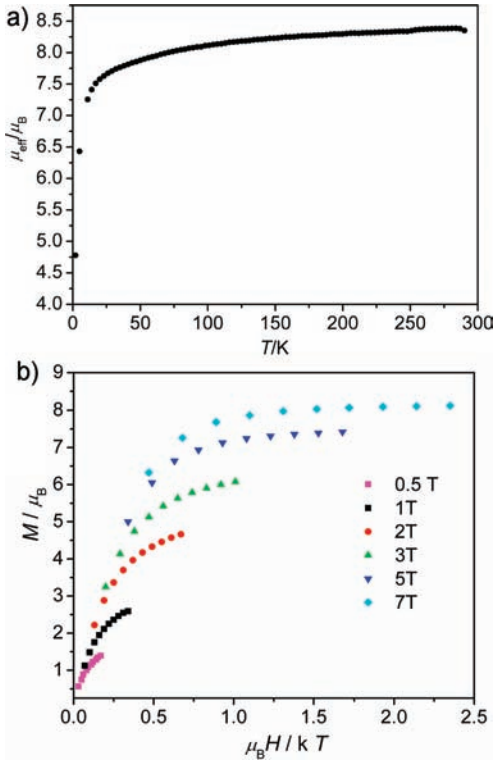
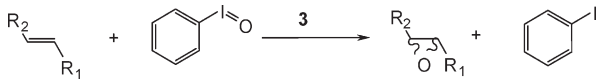


Figure 4. (a) Temperature-dependence of the effective magnetic moment, μ_{eff}, calculated per average Mn^{III}_3 unit in $\mathbf{3^{RR}}\cdot 6H_2O$ at 1 T. (b) Variable-temperature variable-field magnetization measurements calculated per average Mn^{III}_3 unit in $\mathbf{3^{RR}}\cdot 6H_2O$ at 0.5 T, 1 T, 2 T, 3 T, 5 T, and 7 T.

(Figure 4a). From 100 to 20 K, there is a gradual decrease of μ_{eff} value to 7.57 μ_B at 20 K. Below 20 K, the decrease is pronounced with a value of $\mu_{eff} = 4.78\ \mu_B$ at 2 K.

The variable-temperature−variable-field measurements are shown in Figure 4b. The isofield lines show a pronounced nesting behavior indicating energy splitting of the m_s states on the order of the Zeeman splitting. We have analyzed several trinuclear Mn^{III} triplesalen units.[45,46,68] They exhibit antiferromagetic exchange interactions in the range of $J = -0.8$ to $-1.0\ cm^{-1}$ ($H = -2J\boldsymbol{S}_1\boldsymbol{S}_2$) and local zero-field splittings D in the range $3-4\ cm^{-1}$. While the magnetic properties of $\mathbf{3^{RR}}$ indicate an analogous behavior, we refrain from a quantitative analysis due to overparameterization by the presence of two different trinuclear complexes, which possess different J and D values.

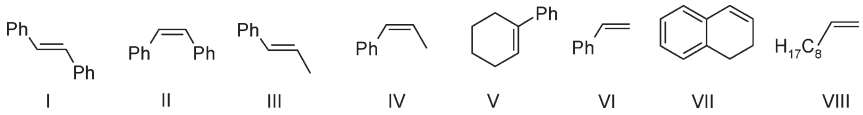
Catalytic Application. We examined the catalytic properties of complex $\mathbf{3^{RR}}$ for the asymmetric epoxidation of olefins. The ofefin and iodosylbenzene (2.75 equiv with respect to the olefin) were added to complex $\mathbf{3^{RR}}$ (5 mol %) in CH_2Cl_2 (2 mL). The mixture was stirred at room temperature for 15 h, and the yield was calculated from the signals of the olefin and the epoxide in the ^1H NMR spectra. The result is tabulated in Table 2. GC and GC-MS results of the olefins as well as the reaction mixtures were recorded. The ^1H NMR and GC measurements show the presence of iodobenzene in the product mixture. This indicates the conversion of iodoslybenzene to iodobenzene during the catalytic cycle according to the following catalytic epoxidation:



The yield and the stereochemistry of the epoxide are highly dependent on the respective substrate. The yields of epoxides were good to excellent using $\mathbf{3^{RR}}$ as a catalyst for the epoxidation reaction. The yield of styrol is 90%. On addition of a methyl group at the β position trans to the phenyl group of styrene, the yield of the corresponding epoxide decreases to 78%. Upon addition of a highly bulky group, like phenyl, at the β position trans to the phenyl group of styrene, the yield of *trans*-stilbene oxide further decreases to 50%. As observed earlier,[24] *cis*-olefins produce a mixture of cis and trans epoxides. Here, the ratio is almost 1:1. The formation of cis and trans epoxides is attributed to stepwise C−O bond formation via a radical intermediate.[11] The decrease of the yield on addition of a bulky substituent may be assigned to a steric effect, which restricts the bulky substrate from reaching the active Mn^V=O site. The enantiomeric excess (ee) is poor for some substrates (I, III, and VI, Table 2). When 1.5 mol % catalyst is used for substrate I, the ee increases to 35%. When the catalysis was carried out at a low temperature (0 °C) for substrate III, there was a slight increase in the ee, 20%, compared to the reaction carried out at room temperature (ee = 8%). Using the enantiomer $\mathbf{3^{SS}}$ as a catalyst for epoxidation of substrate III, almost the same yield of epoxide was obtained. As the absolute configuration of the major epoxide enantiomer was opposite that obtained with $\mathbf{3^{RR}}$, the ee was lower, which might be related to experimental uncertainties.

The yield and the ee in the catalytic asymmetric epoxidation of olefins by Mn^{III} salen complexes may vary strongly with respect to the olefin chosen, the substituents

Table 2. Asymmetric Epoxidation of Olefins by Complex $\mathbf{3}^{\mathbf{RR}}$[a]



alkene	$\mathbf{3}^{\mathbf{RR}}$ (mol %)	yield	ee[b]	absolute configuration[77−79]
I	5	50%[c]	21%	(1S, 2S)
I	1.5	48%[d]	35%	(1S, 2S)
II	5	26% (Z); 20% (E)[e]	13% (E)	(1R, 2R)
III	5	75%[f]	8%	(1R, 2R)
III	5 ($\mathbf{3}^{\mathbf{SS}}$)	76%	2%	(1S, 2S)
III[g]	5	70%[h]	20%	(1R, 2R)
IV	5	32% (Z); 24% (E)[i]	22% (E)	(1R, 2R)
V	1	90%	14%	(1S, 2S)
V	5	90%	56%	(1S, 2S)
VI	5	90%[j]	16%	(1R)
VII	5	78%[k]	33%	(1R, 2S)
VIII	5	18%		

[a] 2.75 equiv of PhIO, room temperature, 15 h, CH_2Cl_2 (solvent). [b] Determined by ^{1}H NMR in the presence of the chiral shift reagent ([Eu(hfc)$_3$]). [c] In addition to 6% benzaldehyde. [d] In addition to 7% benzaldehyde. [e] In addition to 2% benzaldehyde. [f] In addition to 5% benzaldehyde, 5% benzyl methyl ketone. [g] 0 °C, 18 h. [h] In addition to 4% benzyl methyl ketone, 5% benzaldehyde. [i] In addition to 6% benzaldehyde, 6% benzyl methyl ketone. [j] In addition to 7% benzaldehyde, 1% phenyl acetaldehyde. [k] In addition to 15% naphthalene.

on the salen derivative used, and the reaction conditions.[2,69−76] Therefore, it is difficult to compare our results with that of prior publications. It must be noted that we have not optimized the reaction conditions. Overall, the Mn^{III}_3 triplesalen catalyst is slightly better with respect to yield and a bit worse with respect to ee.

Conclusion

We have successfully synthesized the chiral version of triplesalen in both enantiomers: H_6chand^{RR} and H_6chand^{SS}. Reaction with $MnCl_2 \cdot 2H_2O$ yielded the chiral trinuclear triplesalen complexes $\mathbf{3}^{\mathbf{RR}}$ and $\mathbf{3}^{\mathbf{SS}}$, respectively. Crystallographic characterization of both enantiomers provided the presence of the two ionization isomers [(chand){Mn^{III}-Cl(MeOH)}$_3$] and [(chand){Mn^{III}(MeOH)$_2$}$_3$]Cl_3. The crystal structures possess chiral hydrophobic channels. The magnetic properties are in accord with those of previously reported Mn^{III}_3 triplesalen complexes. The chiral trinuclear complexes catalyze the stereoselective epoxidation of unfunctionalized olefins. While the reaction conditions have not been optimized, the catalytic epoxidation shows relatively good yields with lower enantioselectivity in comparison to mononuclear Mn^{III} salen catalysts. Experiments to investigate cooperative effects in catalytic applications are currently performed in our laboratory by competition experiments of functionalized and unfunctionalized substrates. Additionally, the effect in the enentioselective ring-opening of epoxides by going from mononuclear Cr^{III} salen to trinuclear Cr^{III}_3 triplesalen complexes is under investigation.

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Supporting Information Available: Crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.

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