Synthesis, Structural, Spectroscopic, Electrochemical, Magnetic, and Catalytic Properties of the Trinuclear Mn^{III} Triplesalen Complex [(talen^{*t*-Bu₂}){Mn(OAc)}₃] Exhibiting Three Salen-Subunits in a β-*cis*-Conformation

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Abstract. Reaction of the triplesalen ligand H₆talen^{t-Bu₂} with three equivalents Mn(OAc)₂·4H₂O in MeOH results in the formation of a brown solid which upon recrystallization from CH₃CN provides the trinuclear complex [(talen^{t-Bu2}){Mn(OAc)}₃]·7CH₃CN as evidenced by single-crystal X-ray diffraction. The triple tetradentate ligand $(talen^{t-Bu_2})^{6-}$ coordinates to three Mn^{III} ions in the rare β -cisconformation of the salen-like ligand compartments with the central oxygen donor (O^c) being rotated out of the plane. This results in a longer Mn–O^c bond length of 2.00 Å compared to the mean Mn–O^t bond lengths of the terminal phenolates at 1.86 Å. The six-coordination is saturated by bidentate OAc- ligands. The electronic absorption spectrum measured in MeOH appears to be almost identical to all other complexes already studied possessing a $\{(talen^{t-Bu_2})Mn^{III_3}\}^{3+}$ subunit (in the trans-conformation). The spectra measured in CH2Cl2 and CH₃CN exhibit significant variations of the absorption features in the CT region above 20000 cm⁻¹ and a low-energy shift of the d-d transitions from a shoulder around 18000 cm⁻¹ in CH₃OH to maxima around

Introduction

The ligand H₂salen (H₂salen = N,N° -bis(salicylidene)-1,2ethylenediamine) was first reported in 1937 by *Pfeiffer* et al.^[1,2] The ease of its formation by reaction of ethylenediamine with two equivalents of salicylaldehyde, its coordination ability to almost each metal ion, and the ease of tuning its electronic and steric properties by placing substituents at the backbone made it a highly used ligand system (note that modified ligands based on the parent H₂salen backbone will be referred to as salen ligands).^[3,4] A revival of salen ligands and their complexes was initiated by reports of *Jacobson* et al. that chiral Mn^{III} salen complexes are good catalysts for the enantioselective epoxidation of unfunctionalized olefins.^[5,6] These reports initiated worldwide research efforts on the catalytic ability of metal salen complexes. Nowadays, salen complexes of

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 [a] Lehrstuhl für Anorganische Chemie I Fakultät für Chemie, Universität Bielefeld Universitätsstr. 25 33615 Bielefeld, Germany 13000 cm⁻¹ in CH₂Cl₂ and CH₃CN. This indicates a physical dissolution of [(talen^{t-Bu₂}){Mn(OAc)}₃] in CH₂Cl₂ and CH₃CN solutions without major structural rearrangements, while in MeOH solution a structural rearrangement to the preferred trans-conformation of the salen-like coordination compartments occurs loosing the bidentate coordination mode of the OAc⁻ ligands. Electrochemical measurements reveal unresolved irreversible processes in the range 0.9-1.4 V vs. Fc⁺/Fc corresponding to oxidations of the Mn^{III}-phenolate units, while irreversible reductive waves in the range -0.7-(-1.2) V vs. Fc+/Fc correspond to Mn^{III} to Mn^{II} reductions. The analysis of the magnetic data reveals a weaker antiferromagnetic interaction of $J = -0.067 \text{ cm}^{-1}$ and a stronger zero-field splitting of $D = -5.57 \text{ cm}^{-1}$ in comparison to the complexes with $\{(talen^{t-Bu_2})Mn^{III_3}\}^{3+}$ subunits in the *trans*conformation consistent with the longer Mn-Oc distances and the asymmetric coordination environment, respectively. The complex $[(talen^{t-Bu_2}){Mn(OAc)}_3]$ catalyzes the epoxidation of 1,2-dihydronaphthalene with iodosylbenzene with complete conversion at room temperature.

Special Issue

almost any metal ion, irrespective of main group or transition metal, diamagnetic or paramagnetic, has been reported to catalyze an organic transformation.^[7–13]

Besides these catalytic properties, metal salen complexes have been used in molecular magnetism.^[14,15] Especially the magnetic anisotropy of the Mn^{III} salen unit has been utilized for the preparation of molecule-based magnets. For example, *Long* et al. reported trinuclear single-molecule magnets formed by two [(5-Brsalen)Mn^{III}]⁺ building blocks bridged by a [M(CN)₆]^{3–} (M = Cr, Fe).^[16] Dimerized Mn^{III} salen units already exhibit single-molecule magnet properties.^[17] The dimerized building block {[(saltmen)Mn^{III}]₂}²⁺ (H₂saltmen = *N*,*N*^{*}-bis(salicylidene)-1,1,2,2-tetramethyl-1,2-ethylenediamine) has been used for a rational approach to single-chain magnets.^[18,19]

For a rational design of single-molecule magnets, we have developed the C_3 symmetric trinucleating extension of the salen ligand, where three salen subunits are bridged by a central 1,3,5-trihydroxybenzene (phloroglucinol) unit, which we have termed triplesalen (Scheme 1).^[20–23] Due to the unsymmetric diimine units, the parent triplesalen ligand ($\mathbb{R}^1 = \mathbb{R}^2$ =

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 $R^3 = H$) remains elusive, while we have been successful in the synthesis of the triplesalen ligands H_6 talen^R (R = H, NO₂, *t*-Bu).^[20,24] The trinuclear Mn^{III}₃ units [(talen^{*t*-Bu₂})Mn^{III}₃]³⁺ react by molecular recognition with hexacyanometallates to heptanuclear complexes [Mn^{III}₆M^c]ⁿ⁺ (= [{(talen^{*t*-Bu₂})Mn^{III}₃}₂{M^c(CN)₆}]ⁿ⁺).^[25–30] [Mn^{III}₆Cr^{III}]³⁺ is a single-molecule magnet,^[25] which can be prepared as several salts and solvates, which allowed studying the environmental influence on the single-molecule magnet properties.^[29] [Mn^{III}₆Mn^{III}]³⁺ is a single-molecule magnet with hysteretic openings up to ± 10 T.^[28]



Scheme 1.

The synthesis of the [Mn^{III}₆M^c]ⁿ⁺ complexes was performed either by use of $[(talen^{t-Bu_2}){Mn^{III}Cl}_3]$, which has not been crystallized yet, or by the in-situ formation of the molecular building block $[(talen^{t-Bu_2}){Mn^{III}(X)_m}_3]^{n+}$ (X = OAc⁻ or CH₃OH, m = 1 or 2, n = 0, 1, 2 or 3) by the reaction of H₆talen^{t-Bu2} and Mn(OAc)₂•4H₂O in CH₃OH. The nature of this in-situ formed building block remained speculative. Addition of NaBPh₄ resulted in the crystallization of the one-dimensional (1D) coordination polymer {[{(talen^{t-Bu₂})Mn₃(MeOH)}₂(μ_2 -OAc)₃](μ_2 -OAc)}_n(BPh₄)_{2n} $(\{[Mn^{III}_{6}](OAc)\}_{n}(BPh_{4})_{2n})$ made of hexanuclear complexes $[{(talen^{t-Bu_2})Mn_3(MeOH)}_2(\mu_2-OAc)_3]^{3+}$ where two $\{(talen^{t-Bu_2})Mn_3\}^{3+}$ units are bridged by three OAc^{-.[31]} This opened the question whether this hexanuclear complex is the product of a competing reaction, reducing the yield of heptanuclear complexes $[Mn^{III}_{6}M^{c}]^{n+}$ or whether it is only formed under the conditions employing BPh_4^- as counteranion. Herein, we describe the synthesis of the product formed by the reaction of H₆talen^{t-Bu2} and Mn(OAc)₂·4H₂O resulting in $[(talen^{t-Bu_2}){Mn(OAc)}_3]$ with each Mn^{III} ion being sixcoordinate with a bidentate OAc- and the salen subunits in the rare β -*cis*-conformation.^[32] The structural, spectroscopic, electrochemical, and magnetic properties have been investigated and are compared to those of complexes with a $\{(talen^{t-Bu_2})Mn^{III_3}\}^{3+}$ subunit in a *trans*-conformation and its catalytic ability towards the epoxidation of olefins have been tested.

Experimental Section

Preparation of Compounds

 H_6 talen^{*t*-Bu₂} {= 2,4,6-tris{1-[2-(3,5-di-*tert*-butylsalicylaldimino)-2-methylpropylimino]-ethyl}-1,3,5-trihydroxybenzene} was synthesized as described previously.^[24]

[(talen^{t-Bu₂}){Mn^{III}(OAc)}₃]. A suspension of H₆talen^{t-Bu₂} (666 mg, 0.599 mmol) and Mn(OAc)₂·4H₂O (444 mg, 1.81 mmol) in CH₃OH (200 mL) was heated with exposure to air at reflux for 45 minutes. The resulting brown solution was cooled to room temperature and filtered. Slow evaporation of the solvent to dryness resulted in a darkbrown residue. This was suspended in CH₃CN (150 mL), stirred for 15 minutes, and filtered. Slow evaporation of the filtrate afforded large brown crystals. The product was identified crystallographically as $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ ·7CH₃CN. The other measurements were performed on air-dried samples. Several elemental analyses indicated the complete loss of the non-coordinated CH₃CN molecules and incorporation of water. Yield: 300 mg (29%). ESI-MS (MeOH): m/z: 664.3 [(talen^{t-Bu₂})Mn₃(OAc)]²⁺ (calcd. 664.3), 1363.6 [(talen^{*t*-Bu₂})Mn₃(OAc)(OH)(H₂O)]⁺ (calcd. 1363.6). IR (KBr): \tilde{v} (cm⁻¹) = 2953m, 2905m, 2868m, 1616s, 1555s, 1478vs, 1431m, 1395m, 1364m, 1341m, 1310m, 1275s, 1254s, 1192m, 1163m, 1145m, 1026w, 845m, 820w, 779w, 750w, 640w, 575w, 548m. Elemental analysis (%): calcd. for $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ ·4.2H₂O $(C_{75}H_{113,4}N_6O_{12,2}Mn_3)$: C 59.14, H 7.50, N 5.52; found: C 58.80, H 7.43, N 5.48 %.

General Procedure for Catalytic Reactions

The complex $[(talen'^{-Bu_2}){Mn^{III}(OAc)}_3]$ (18 mg, 0.010 mmol) was dissolved in CH₂Cl₂ (4 mL). To this solution 1,2-dihydronaphthalene (26 mg, 0.20 mmol) and iodosylbenzene (122 mg, 0.555 mmol) were added and stirred at room temperature for 16 hours. The solvent was evaporated and the residue treated with CH₂Cl₂ (2 mL) and passed through a short SiO₂ column. The column was washed with CH₂Cl₂ (60 mL). The resulting solution was evaporated and ¹H NMR spectra were recorded after dissolving the residue in CDCl₃ (0.6 mL).

X-ray Crystallography

Structure determination for $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ ·7CH₃CN: M =1734.85 g·mol⁻¹, C₈₉H₁₂₆Mn₃N₁₃O₁₂, triclinic, space group $P\bar{1}$, a =15.2562(6), b = 15.9788(6), c = 21.9324(9) Å, a = 73.1530(10), $\beta =$ 76.433(2), $\gamma = 68.9390(10)^{\circ}$, V = 4724.1(3) Å³, Z = 2, $\rho = 1.220$ g·cm⁻³, $\mu = 3.716 \text{ mm}^{-1}$, F(000) = 1844, crystal size = 0.46 \times 0.45 \times 0.27 mm³. Brown crystals of [(talen^{*t*-Bu₂}){Mn^{III}(OAc)}₃]•7CH₃CN were removed from the mother liquor and immediately cooled to 100(2) K with a Bruker Kappa APEX II diffractometer (four circle goniometer with 4K CCD detector, Mo- K_{α} radiation, focussing graphite monochromator; ω - and ϕ -scans). A total of 52494 reflections $(2.13 < \Theta < 66.61^{\circ})$ were collected of which 15855 reflections were unique (R(int) = 0.0274). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2008/1.^[33] The structure was solved with the program SHELXS-97^[34] and refined using SHELXL-97^[34] to R = 0.0346 for 15387 reflections with $I > 2\sigma(I)$, R = 0.0356 for all reflections; max/min residual electron density 0.621 and -0.411 e·Å⁻³.

CCDC-924347 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Other Physical Measurements

Infrared spectra (400–4000 cm⁻¹) of solid samples were recorded on a Shimadzu FT-IR 8400S as KBr disks. ESI mass spectra were recorded with a Bruker Esquire 3000 ion trap mass spectrometer. Elemental analyses were carried out on a LECO CHN-932 or a HEKAtech Euro



EA elemental analyzer. UV/Vis/NIR absorption spectra of solutions were measured with a Shimadzu UV-3101PC spectrophotometer in the range 190-3200 nm at ambient temperatures. The electrochemical experiments were performed on Ar-flushed MeCN solutions containing 0.1 M [NBu₄]PF₆ in a classical three-electrode cell. The working electrode was a glassy carbon disk electrode, the counter electrode a platinum wire, and the reference electrode was Ag/0.01 M AgNO₃ MeCN. All potentials are referenced to the ferrocenium/ferrocene (Fc+/Fc) couple used as an internal standard. The electrochemical cell was connected to an EG&G potentiostat/galvanostat model 273A. Temperature-dependent magnetic susceptibilities were measured by using a SQUID magnetometer (MPMS XL-7 EC, Quantum Design) in a static field of 1 T in the range 2-290 K. Variable-temperature variable-field (VTVH) measurements were performed in various static fields (1-7 T) in the range 2-10 K with the magnetization equidistantly sampled on a 1/T temperature scale. For calculations of the molar magnetic susceptibilities, χ_m , the measured susceptibilities were corrected for the underlying diamagnetism of the sample holder and the sample by using tabulated Pascal's constants.

Results and Discussion

Synthesis and Characterization

The synthesis of the heptanuclear complexes $[Mn^{III}_{6}M^{c}]^{n+1}$ starts with the reaction of H₆talen^{t-Bu2} with 2.8 equivalents of Mn(OAc)₂·4H₂O in CH₃OH, followed by heating the mixture at reflux.^[29,30] It is thought that by air oxidation the molecular building block $[(talen^{t-Bu_2}) \{ Mn^{III}(X)_m \}_3]^{n+}$ (X = OAc⁻ or MeOH, m = 1 or 2, n = 0, 1, 2 or 3) is formed, which is insitu reacted with a hexacyanometallate. The slight Mn deficit is important to suppress the formation of Prussian blue analogs of unreacted Mn ions upon addition of the hexacyanometallate.^[29,30] Addition of a solution of NaBPh₄ instead of hexacyanometallate allowed the isolation the of $[Mn^{III}_{6}](OAc)\}_{n}(BPh_{4})_{2n}.^{[31]}$

In order to better understand the in-situ formed trinuclear building block for the preparation of $[Mn^{III}_{6}M^{c}]^{n+}$, we have reacted H₆talen^{t-Bu2} in CH₃OH with 3.02 equivalents Mn(OAc)₂·4H₂O and heated at reflux. The resulting complex is highly soluble in CH₃OH so that upon slow evaporation of the solvent an impure product could only be isolated upon complete evaporation of the solvent. Recrystallization from CH₃CN provided well-shaped brown crystals, which were analyzed by single-crystal X-ray diffraction as [(talen^{t-Bu₂}){Mn^{III}(OAc)}₃]•7CH₃CN. Surprisingly, the FT-IR spectra provide no indication of the co-crystallized CH₃CN molecules. This is corroborated by several elemental analyses. The formulation including seven CH₃CN molecules of crystallization corresponds to a nitrogen content of 10.50%, while the measured nitrogen content of approx. 5.5 % indicates the complete loss of the co-crystallized CH₃CN molecules. Moreover, the desolvated samples appear to be hygroscopic and the amount of water molecules per formula unit depends on the time-span between isolation of the crystals and elemental analysis.

The FT-IR spectra are governed by the intense vibration of the ligand backbone. Small variations to the FT-IR of $[(talen^{t-Bu_2})\{Mn^{III}Cl\}_3]$ and $\{[Mn^{III}_6](OAc)\}_n(BPh_4)_{2n}$ do not

allow speculations on different coordination modes of the acetate as the BPh₄⁻ counteranion in {[Mn^{III}₆](OAc)}_n(BPh₄)_{2n} some additional intensity. ESI-MS provides of [(talen^{t-Bu₂}){Mn^{III}(OAc)}₃] dissolved in MeOH provides intense signals corresponding to $[(talen^{t-Bu_2})Mn^{III}_3(OAc)_2]^{2+}$ and [(talen^{*t*-Bu₂})Mn^{III}₃(OAc)(OH)(OH₂)]⁺ indicating that the coordinated OAc⁻ ligands may dissociate in methanolic solution. On the other hand, CH₃CN solutions neither provide characteristic peaks of the complex nor of complex fragments. This is consistent with the charge neutrality of the undissociated molecule and a lower dissociation tendency of the coordinated OAc⁻ in CH₃CN solutions compared to MeOH solutions.

Structural Characterization

The compound crystallizes in the space group $P\bar{1}$ with one formula unit in the asymmetric unit. The molecular structure of [(talen^{t-Bu₂}){Mn^{III}(OAc)}₃] is provided in Figure 1 and selected interatomic distances and angles in Table 1. The trinuclear complex is comprised of one triple tetradentate ligand (talen^{t-Bu2})⁶⁻ that coordinates three Mn^{III} ions. Each Mn^{III} ion is six-coordinate with a bidentate OAc⁻ saturating the coordination sphere. The coordination polyhedron can only merely be described as distorted octahedral as evidenced by angles in the range 144–173° for *trans*-standing ligands and 57–124° for cis-standing ligands. This irregular coordination can be related to the small bit-angle (approx. 58°) of the bidentate OAc⁻ that enforces a β -cis-conformation^[32] of the salen-like ligand compartments instead of its preferred trans-conformation.^[4] The oxygen donor atoms O^c of the central phloroglucinol backbone (O11, O21, O31) are rotated out of the $MnO'N_2$ plane.



Figure 1. Molecular structure of $[(talen^{r-Bu_2}){Mn^{III}(OAc)}_3]$ in crystals of $[(talen^{r-Bu_2}){Mn^{III}(OAc)}_3]$ ·7CH₃CN and numbering scheme used. Hydrogen atoms have been omitted for clarity.

This irregular coordination polyhedron is also manifested in the bond lengths. A proper comparison is provided by $[Mn^{III}_{6}]^{3+,[31]}$ which has a *trans*-conformation of the salen-

Table 1. Selected interatomic distances /Å and angles /deg for [(talen^{*t*-Bu₂}){ $Mn^{III}(OAc)$ }]·7CH₃CN.

Mn1-012	1.8494(11)	C301-C302	1.413(2)
Mn1-011	2.0022(11)	C302-C303	1.403(2)
Mn1-N11	1.9654(13)	C303-C304	1.385(2)
Mn1-N12	2.0038(13)	C304-C305	1.400(2)
Mn1-0401	2.0433(11)	C305-C306	1.389(2)
Mn1-0411	2.3776(12)	C301-C306	1.424(2)
Mn2-O21	1.9693(11)		
Mn2-O22	1.8654(11)	O12-Mn1-N11	173.40(5)
Mn2-N21	1.9694(13)	O12-Mn1-O11	94.52(5)
Mn2-N22	2.0414(13)	N11-Mn1-O11	84.09(5)
Mn2-0412	2.1766(11)	O12-Mn1-N12	91.24(5)
Mn2-0402	2.2623(13)	N11-Mn1-N12	83.02(5)
Mn3-O31	2.0155(11)	O11-Mn1-N12	106.80(5)
Mn3-O32	1.8562(11)	O12-Mn1-O401	92.69(5)
Mn3-N31	1.9729(13)	N11-Mn1-O401	93.90(5)
Mn3-N32	2.0167(12)	O11-Mn1-O401	100.18(5)
Mn3-0413	2.0274(12)	N12-Mn1-O401	152.33(5)
Mn3-0403	2.4797(13)	O12-Mn1-O411	96.21(5)
Mn1–Mn2	7.1929(4)	N11-Mn1-O411	87.42(5)
Mn1–Mn3	6.8520(4)	O11-Mn1-O411	156.83(4)
Mn2–Mn3	7.2997(4)	N12-Mn1-O411	93.45(5)
011–C1	1.2875(19)	O401-Mn1-O411	58.89(4)
O21–C3	1.3070(18)	O12–Mn1–Mn3	81.48(4)
O31–C5	1.3003(18)	N11–Mn1–Mn3	100.18(4)
O12-C101	1.315(2)	Oll-Mnl-Mn3	30.39(3)
O22-C201	1.3261(19)	N12–Mn1–Mn3	134.11(4)
O32-C301	1.3274(19)	O401–Mn1–Mn3	73.54(3)
0401–C401	1.280(2)	O411–Mn1–Mn3	132.27(3)
0411–C401	1.247(2)	022-Mn2-021	92.89(5)
0402–C402	1.258(2)	O22-Mn2-N21	169.69(5)
0412–C402	1.265(2)	O21 - Mn2 - N21	86.34(5)
0403 - C403	1.241(2) 1.281(2)	O22-Min2-N22 O21-Min2-N22	90.02(5)
0413-C403	1.281(2) 1.201(2)	O21-Min2-N22 N21 $Min2$ N22	124.02(3)
N12 C17	1.301(2) 1.200(2)	$M_{21} = M_{112} = M_{22}$	01.93(3)
N12-C17	1.290(2) 1.306(2)	O22 - Mn2 - O412 O21 Mn2 O412	93.43(4) 01.21(4)
N22 C27	1.300(2) 1.282(2)	$M_{21} = M_{12} = 0.412$	91.31(4) 04.84(5)
N22-C27	1.202(2) 1.302(2)	N21 - M12 - O412 N22 Mn2 O412	1/3 07(5)
N31-C31	1.302(2) 1.288(2)	$\Omega_{22} = Mn_2 = O_{412}$	145.97(5) 03.65(5)
C1 - C2	1.200(2) 1.434(2)	O22=Mn2=O402 O21=Mn2=O402	$150\ 11(4)$
$C_{1}-C_{2}$	1.434(2) 1.425(2)	N21_Mn2_0402	$92 \ 10(5)$
$C_{3}-C_{4}$	1.423(2) 1.431(2)	N22_Mn2_0402	85 13(5)
C4-C5	1.437(2)	O412 - Mn2 - O402	59.04(4)
C1-C6	1.430(2)	O32-Mn3-N31	171.79(5)
C5-C6	1.411(2)	O32-Mn3-O31	93.28(4)
C2-C11	1.457(2)	N31-Mn3-O31	86.37(5)
C4-C21	1.452(2)	O32-Mn3-N32	90.57(5)
C6-C31	1.456(2)	N31-Mn3-N32	82.33(5)
C101-C102	1.415(2)	O31-Mn3-N32	117.24(5)
C102-C103	1.409(2)	O32-Mn3-O413	92.96(5)
C103-C104	1.377(2)	N31-Mn3-O413	95.23(5)
C104–C105	1.408(2)	O31-Mn3-O413	96.52(5)
C105-C106	1.381(2)	N32-Mn3-O413	145.79(5)
C101–C106	1.428(2)	O32-Mn3-O403	94.24(5)
C201–C202	1.417(2)	N31-Mn3-O403	89.70(5)
C202–C203	1.408(2)	O31-Mn3-O403	153.10(5)
C203-C204	1.378(2)	N32-Mn3-O403	88.48(5)
C204–C205	1.408(2)	O413-Mn3-O403	57.33(5)
C205-C206	1.383(2)		
C201-C206	1.426(2)		

like ligand compartments with a OAc^- and a MeOH in the axial coordination sites. The mean Mn–O^c bond lengths at 2.00 Å are much longer than the mean Mn–O^t bond lengths at 1.86 Å, which is close to the value of 1.88 Å for the Mn–O^t

and Mn–O^{*c*} bond lengths in $[Mn^{III}_6]^{3+,[31]}$ Additionally, the mean Mn–N^{*t*} distance at 2.02 Å is longer than that for Mn–N^{*c*} at 1.97 Å, which corresponds to the Mn–N^{*t*} and Mn–N^{*c*} bond lengths in $[Mn^{III}_6]^{3+,[31]}$

A common feature of the extended phloroglucinol ligands and their complexes is the heteroradialene formation of the central ligand backbone, which is not best described by an aromatic 1,3,5-hydroxy-2,4,6-triimine-benzene resonance structure but a cross-conjugated (i.e. not aromatic) 1,3,5-triketo-2,4,6-trienamine-cyclohexane resonance structure.^[23,29,30,35–40] is also This evidenced in $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ by the large mean $C^{ar}-C^{ar}$ bond length of 1.43 Å compared to 1.40 Å for the terminal phenolates and a shortening of the mean C-O^c bond length of 1.30 Å compared the mean C–O^t bond length of 1.33 Å.

Electronic Absorption Spectroscopy

The electronic absorption of spectrum $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ has been measured in CH₃CN, CH₂Cl₂, and MeOH solutions (Figure 2). The spectral features with a steadily increasing absorption intensity starting in the 10000–15000 cm⁻¹ region up to ε values of 80 \times 10³ M⁻¹ cm⁻¹ around 45000 cm⁻¹ are characteristic for complexes with $\{(talen^{t-Bu_2})Mn^{III_3}\}^{3+}$ subunits.^[29,30] It should be noted that the absorption features differ for the three solutions. The absorption features and maxima in the non-coordinating solvent CH₂Cl₂ and in CH₃CN, which is a potentially coordinating solvent but untypical donor for Mn^{III}, almost coincide, while for the polar and coordinating solvent MeOH the absorption features differ significantly. The absorptions above 20000 cm⁻¹ have been assigned to CT transitions and transitions involvthe central heteroradialene backbone.^[29,30] ing In [Mn^{III}₆Cr^{III}]³⁺, a shoulder around 18000 cm⁻¹ has been analyzed in detail and assigned to the Mn^{III} d-d transitions.^[29] Interestingly, the spectrum of $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ measured in MeOH exhibits the same kind of shoulder around 18000 cm⁻¹, while this feature is shifted to lower energy with maxima at 13200 cm⁻¹ ($\varepsilon = 1720 \text{ m}^{-1} \text{ cm}^{-1}$) in CH₃CN and at 12900 cm^{-1} ($\varepsilon = 1720 \text{ M}^{-1} \text{ cm}^{-1}$) in CH₂Cl₂. Solvatochromic effects are usually more significant for CT transitions as the redistribution of electron density between the ground state and the CT excited states experience a different interaction with the surrounding solvents in comparison to d-d transitions, where the electronic redistribution is mainly located at a metal ion, which is not directly exposed to solvent molecules. In this respect, the almost identical d-d transitions and the almost identical absorption features in the CT region implies that the molecular structure in CH₃CN and CH₂Cl₂ varies only minorly, while the molecular structure in MeOH solution differs significantly. These results are consistent with a pure dissolution in the non- or only weakly coordinating solvents CH₃CN and CH_2Cl_2 , remaining the β -cis-conformation of the salenlike ligand compartments and bidentately coordinated OAcligands, while in MeOH solution the OAc- ligands do not coordinate bidentately, resulting in the usual trans-conformation of the salen-like ligand compartments. This interpretation is



corroborated by a comparison to the spectrum of $[(talen^{t-Bu_2}){Mn^{III}(X)_m}_3]^{n+}$ (X = OAc⁻ or MeOH, m = 1 or 2, n = 0, 1, 2 or 3) in MeOH, which has been prepared in-situ by reaction of H₆talen^{t-Bu_2} with three equivalents Mn(OAc)₂· 4H₂O (light solid spectrum in Figure 2). These species in MeOH should feature *trans*-coordinated salen-like coordination compartments with MeOH and/or OAc⁻ ligands in the axial coordination sites. Thus, the complex dissolves physically in CH₃CN and CH₂Cl₂ solution, while a reorganization of the Mn^{III} environment occurs in MeOH solution.



Figure 2. Electronic absorption spectra of $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ measured on CH₃CN, CH₂Cl₂, and CH₃OH solutions. For comparison, the spectrum of $[(talen^{t-Bu_2}){Mn^{III}(X)_m}_3]^{n+}$ (X = OAc⁻ or CH₃OH, m = 1 or 2, n = 0, 1, 2 or 3) as generated in-situ in CH₃OH^[52] is included. The inset shows the d-d transitions.

Electrochemistry

As the electronic absorption spectra indicate that the overall molecular structure of [(talen^{t-Bu₂}){Mn^{III}(OAc)}₃] remains in CH₃CN solution, the electrochemistry has been studied in CH₃CN solutions by cyclic (CV, Figure 3) and square-wave (SW) voltammetry. Non-resolved redox events are observed at positive potentials with peak potentials at 0.96, 1.16, and 1.38 V (all potentials are referenced to the Fc⁺/Fc couple), that are not reversible. Analogous oxidative waves have been observed in $[Mn^{III}_{6}Cr^{III}]^{3+}$ [29] and $[Mn^{III}_{6}Mn^{III}]^{3+}$, [30] while even mononuclear Mn^{III} salen complexes exhibit oxidation processes in a range of 0.2 to 0.9 V depending on the specific salen-type ligand and the ligands in the axial coordination sites.^[41] As these oxidations are irreversible, we refrain from an assignment either to a metal-centered oxidation leading to Mn^{IV} species or to ligand-centered oxidations leading to coordinated phenoxyl radical species. In the trinuclear Ni^{II}₃ ^[24] and Cu^{II}₃ ^[42] triplesalen complexes, some of these oxidations are reversible and have been studied according to the nature of the oxidized species. At negative potentials, there are three unresolved reductive electron transfer waves with peak potential at -0.78, -0.98, and -1.21 V, where some current for the reoxidation can be observed. However, the SW data clearly indicate that these processes are also irreversible. Again, analogous reductions are observed in [Mn^{III}₆Cr^{III}]^{3+ [29]} and [Mn^{III}₆Mn^{III}]³⁺.^[30] Mononuclear Mn^{III} salen complexes have been reported to exhibit reversible and irreversible reduction processes between -0.7 and +0.3 V, which has been assigned to the reduction of Mn^{III} to Mn^{II,[41,43,44]} which therefore also appears feasible for the three reductions in [(talen^{*t*-Bu₂}){Mn^{III}(OAc)}₃].



Figure 3. Cyclic voltammograms of $[(talen^{r-Bu_2}){Mn^{III}(OAc)}_3]$ -7CH₃CN in CH₃CN solution (0.1 M [NBu₄]PF₆) recorded at a glassy carbon working electrode at 20 °C.

Magnetic Measurements

Magnetic susceptibility data of $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ were measured on a microcrystalline sample in the temperature range 2–290 K with an applied field of 1 T. Above 100 K, the effective magnetic moment, μ_{eff} , is almost constant with 8.47 ± 0.01 μ_B . Below 100 K, there is a slight decrease of μ_{eff} to a value of 5.26 μ_B at 2 K (Figure 4). We have analyzed the magnetic properties of $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ using the appropriate spin Hamiltonian (1) for three coupled spins $S_i = 2$ including the isotropic Heisenberg–Dirac–van Vleck (HDvV) exchange Hamiltonian, the single-ion zero-field splitting, and the single-ion Zeeman interaction.^[45]

$$H = -2J(\mathbf{S}_{1}\mathbf{S}_{2} + \mathbf{S}_{2}\mathbf{S}_{3} + \mathbf{S}_{3}\mathbf{S}_{1}) + \sum_{i=1}^{3} \left[D\left(\hat{S}_{zi}^{2} - \frac{1}{3}S_{i}(S_{i}+1)\right) + \mu_{B}\mathbf{S}_{i}\mathbf{g}\mathbf{B} \right]$$
(1)

The dotted line in Figure 4 corresponds to an uncoupled system (J = 0) of isotropic spins (D = 0), which does not reproduce the temperature-dependence below 100 K. Using an anti-ferromagnetic coupling that is typical for $\{(\text{talen}^{t-\text{Bu}_2})\text{Mn}^{\text{III}}_3\}^{3+}$ units in *trans*-conformations $(J = -0.8 \text{ cm}^{-1}, ^{[23]}$ dash dotted line in Figure 4) clearly demonstrate that the coupling in $[(\text{talen}^{t-\text{Bu}_2})\{\text{Mn}^{\text{III}}(\text{OAc})\}_3]$ is less strong, even less strong than $J = -0.2 \text{ cm}^{-1}$ (dash-dot-dotted line in Figure 4). Using an uncoupled behavior but zero-field splittings, a value of $D = -8 \text{ cm}^{-1}$ is necessary to provide a rough reproductions of the experimental data. However, such a strong magnetic an-



Figure 4. Temperature-dependence of the effective magnetic moment, $\mu_{\rm eff}$, of [(talen^{*t*-Bu₂}){Mn^{III}(OAc)}₃] at 1 T. The solid lines are simulations to the experimental data using the spin-Hamiltonian provided in the text. The values are all in cm⁻¹.

isotropy seems not feasible for Mn^{III} h.s.^[46–49] Fitting of the experimental data taking into account a small antiferromagnetic coupling and a zero-field splitting provided $J = -0.067 \text{ cm}^{-1}$ and $D = -5.57 \text{ cm}^{-1}$ (bold solid line in Figure 4). It should be noted that VTVH data cannot be well reproduced at all using the applied model that implies colinearly oriented zero-field splitting tensors. As has been demonstrated previously,^[26,27,29–31] a meaningful simulation of VTVH data for such a highly anisotropic system requires that the relative orientations of zero-field splitting tensors are considered which is beyond the scope of this study.

Nevertheless, the presence of strongly reduced antiferromagnetic interactions and a more pronounced magnetic anisotropy can still be deduced from the magnetic analysis. The small antiferromagnetic interaction is in accordance to the longer Mn–O^c bond lengths implying a smaller covalency and thus weaker exchange pathways through the central phloroglucinol backbone. Furthermore, the highly asymmetric coordination environment in [(talen^{*t*-Bu₂}){Mn^{III}(OAc)}₃] compared to {(talen^{*t*-Bu₂})Mn^{III}₃}³⁺ subunits in *trans*-conformations may be accounted for by the strong magnetic anisotropy, which might be slightly smaller by a more elaborated analysis.

Catalytic Properties

order to test the catalytic ability In of $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ in the epoxidation of olefins, we employed 1,2-dihydronaphthalene as a model substrate^[50] under the same conditions of our more detailed study using the chiral trinuclear Mn^{III}₃ triplesalen complexes $[(chand^{RR}){Mn^{III}Cl(CH_3OH)}_3]$ and [(chand^{SS}){Mn^{III}Cl- $(CH_3OH)_3$ $(H_6chand^{RR} = 2,4,6-tris\{1-[(1R,2R)-2-(3,5$ di-tert-butylsalicylaldimino)cyclohexylimino]ethyl}-1,3,5trihydroxybenzene and H_6 chand^{SS} = 2,4,6-tris{1-[(1*S*,2*S*)-2-(3,5-di-tert-butylsalicylaldimino)cyclohexylimino]ethyl}-1,3,5-trihydroxybenzene).^[51] 1,2-Dihydronaphthalene and iodosylbenzene (2.78 eqv. with respect to the olefin) were added to $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ (5 mol-%) in CH_2Cl_2 (Scheme 2). The mixture was stirred at room temperature for 16 hours and analyzed by ¹H NMR spectroscopy. Under these conditions, no signal of the substrate 1,2-dihydronaphthalene can be detected indicating complete conversion. The spectra exhibit the signals of 1,2-dihydronaphthalene oxide and naphthalene (19%, mean value of three independent runs). Using [(chand^{RR}){Mn^{III}Cl}₃] 93% conversion with 15% naphthalene was observed.^[51] These results indicate that [(talen^{*t*-Bu₂}){Mn^{III}(OAc)}₃] is a good catalyst for the epoxidation of olefins.





Summary

The triplesalen ligand H₆talen^{t-Bu₂} has been reacted with three equivalents Mn(OAc)2·4H2O in CH3OH in order to obtain more information on the in-situ formed molecular building block for the preparation of the heptanuclear complexes $[Mn^{III}_{6}M^{c}]^{n+}$. In an earlier report, we described the isolation of an insoluble 1D chain compound upon addition of NaBPh₄ that consists of hexanuclear complexes $[\{(talen^{t-Bu_2})Mn_3(MeOH)\}_2(\mu_2-OAc)_3]^{3+}$ where two $\{(talen^{t-Bu_2})Mn_3\}^{3+}$ sub-units are bridged by three OAc⁻. Without the addition of a suitable counter-anion, no precipitate occurs prior to the complete evaporation of the solvent. Recrystallization of this residue from CH₃CN provides the trinuclear complex $[(talen^{t-Bu_2}){Mn(OAc)}_3]$. Unlike all other complexes possessing $\{(talen^{t-Bu_2})Mn_3\}^{3+}$ sub-units, the triple tetradentate ligand (talen^{t-Bu2})⁶⁻ coordinates to three Mn^{III} ions in the rare β -*cis*-conformation of the salen-like ligand compartments with the central oxygen donors being rotated out of the plane. The six-coordination is saturated by bidentate OAc- ligands. This unusual coordination mode results in an elongation of the central Mn–O^c bond lengths of 2.00 Å compared to 1.88–1.89 Å of the conventional $\{(talen^{t-Bu_2})Mn_3\}^{3+}$ sub-units with trans-conformation.

This unusual coordination mode is also reflected in the magnetic properties of the complex. The longer Mn–O^c distances results in weaker antiferromagnetic interactions of $J = -0.067 \text{ cm}^{-1}$ compared to $J = -0.8 \text{ cm}^{-1}$ observed in $[\mathbf{Mn^{II}}_{6}\mathbf{M}^{c}]^{n+}$. The asymmetric coordination environment may be accounted for the strong zero-field splitting of $D = -5.57 \text{ cm}^{-1}$ in comparison to $D = -2.5 \text{ to } -4.0 \text{ cm}^{-1}$ in complexes with {(talen^{t-Bu₂})Mn^{III}₃}³⁺ sub-units in the *trans*-conformation.

Solution studies by ESI-MS and electronic absorption spectroscopy provides strong evidence that this unusual coordination mode prevails in CH_2Cl_2 and CH_3CN solutions while in CH_3OH solution the bidentate OAc^- coordination is lost and the salen-like ligand compartments are back in the usual *trans*-conformation. The electrochemical study in CH_3CN solution provides several irreversible oxidative and reductive waves that have counterparts in complexes with the



The complex $[(talen^{t-Bu_2}){Mn(OAc)}_3]$ appears to be a good catalyst for the epoxidation of unfunctionalized olefins. This study indicates that the in-situ formed building block in CH₃OH is not $[(talen^{t-Bu_2}){Mn^{III}(OAc)}_3]$ with a β -*cis*-conformation but it must consists of a *trans*-conformation. However, this study does not provide evidence whether this building block is a trinuclear $[(talen^{t-Bu_2}){Mn^{III}(X)_m}_3]^{n+}$ (X = OAc⁻ or MeOH, m = 1 or 2, n = 0, 1, 2 or 3) unit or a dimerized hexanuclear $[\{(talen^{t-Bu_2})Mn_3(MeOH)\}_2(\mu_2$ -OAc)_3]^{3+} unit.

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