Synthesis of a Cofacial Schiff-Base Dimanganese(III) Complex for Asymmetric Catalytic Oxidation of Sulfides

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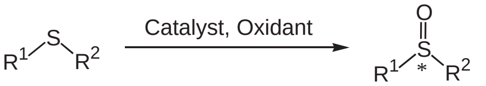
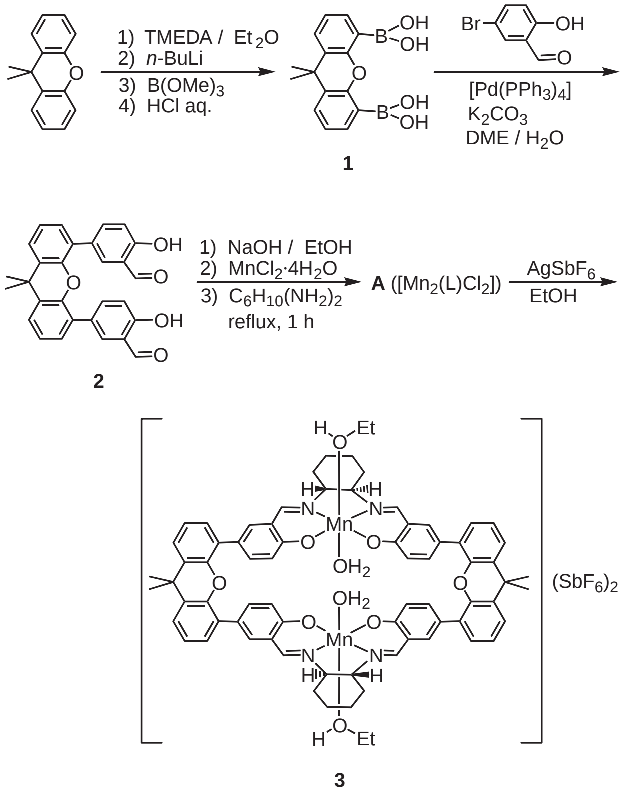
An optically active dimanganese(III) complex was synthesized by a template reaction of 5,5′-(9,9-dimethylxanthene-4,5-diyl)bis(salicylaldehyde), (1*R*,2*R*)-1,2-cyclohexanediamine, and $MnCl_2$, in which two manganese(III) Schiff-base units are cofacially arranged by two 9,9-dimethylxanthenediyl spacers. The dimanganese complex catalyzed the asymmetric oxidation of methyl phenyl sulfide by iodosobenzene.

Asymmetric oxidation of sulfides is a key reaction for synthesis of biologically active compounds with chiral sulfoxide centers.[1] It has been reported that optically active salen-type Schiff-base manganese(III) complexes are efficient catalysts for the asymmetric oxidation of sulfides (Eq 1).[2] However, the enantioselectivity is not high enough for synthetic applications. Design of chiral macrocyclic dinuclear complexes would be a good approach to efficient asymmetric catalysts, because two metal centers are expected to behave cooperatively as an enantioselective Lewis-acid center to catch a sulfide and an active oxidation site upon sulfoxidation, respectively. Among macrocyclic Schiff-base complexes, face-to-face salen-type complex dimers have been limited to a few systems.[3] In this work, we report a new catalyst, optically active Schiff-base manganese(III) complex dimer **3** (Scheme 1). The two Schiff-base manganese(III) units in **3** are doubly bridged by two 9,9-dimethylxanthenediyl spacers to form a cofacial structure.



(1)

Complex **3** was synthesized via 5,5′-(9,9-dimethylxanthene-4,5-diyl)bis(salicylaldehyde) (**2**) as summarized in Scheme 1. Twofold lithiation of 9,9-dimethylxanthene followed by the boronation and hydrolysis afforded 9,9-dimethylxanthene-4,5-diboronic acid (**1**) in 50% yield.[4,5] Palladium-catalyzed cross-coupling reaction of **1** with 2 equiv. of 5-bromosalicylaldehyde gave **2** in 70% yield.[6,7] The structure of **2** was determined by X-ray analysis (Figure 1).[7] Two salicylaldehyde moieties are almost parallel and anchored by 9,9-dimethylxanthene-4,5-diyl unit to form a U-shaped molecule. The interatomic distance of two terminal phenol oxygen atoms (O2···O4, 4.780(5) Å) is comparable to that of the two carbon atoms (C1···C7, 4.675(4) Å). Dihedral angles between the phenyl planes of salicylaldehydes and the xanthene plane are not perpendicular but 49.7(1) and 42.7(1)°. The interplane separation of two salicylaldehyde units (C16···C29, 3.332(5) Å) is smaller than the C1···C7 distance (4.675(4) Å) owing to the small dihedral angles.



Scheme 1.

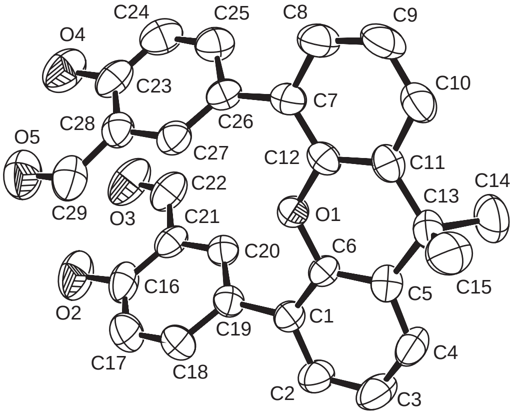


Figure 1. ORTEP drawing of **2** (thermal ellipsoids at the 50% probability level).

The dimeric manganese(III) Schiff-base complex was synthesized by a template reaction of **2**, (1*R*,2*R*)-1,2-cyclohexanediamine, and Mn^{2+} ions. The 1:1 mixture of **2** and $MnCl_2·4H_2O$ was reacted with (1*R*,2*R*)-1,2-cyclohexanediamine in ethanol to give **A** as a brown precipitate. The electrospray-ionization mass spectrum of **A** in methanol showed two clusters of peaks at m/z 581.4 and 1197.4. The observed molecular mass numbers and the isotopic distribution patterns of these peaks match well with those of $[Mn_2(L)]^{2+}$ and $[Mn_2(L)Cl]^+$, respectively. These data and poor solubility of the product suggest that **A** contains the neutral dimanganese complex $[Mn_2(L)Cl_2]$. To improve the solubility, successive reaction of **A** with $AgSbF_6$ in ethanol was carried out to give $[Mn_2(L)(EtOH)_2(H_2O)_2](SbF_6)_2$ (**3**) as brown crystals (18% yield based on **2**).[8] The CD spectral pattern of **3** was similar to that of the corresponding mononuclear complex [Mn(salchxn)Cl] (**4**: H_2salchxn = (1*R*,2*R*)-bis(salicylidene)-1,2-cyclohexanediamine) without the xanthenediyl spacers. The electrospray-ionization mass spectrum of **3** in CH_3CN showed two clusters of peaks at m/z 581.4 and 1197.4 which are assignable to $[Mn_2(L)]^{2+}$ and $[Mn_2(L)(H_2O)(OH)]^+$, respectively.

In contrast to the template reaction using Mn^{2+} ions described above, the 1:1 reaction of **2** and (1*R*,2*R*)-1,2-cyclohexanediamine gave a complex mixture. The desired 2 + 2 Schiff-base condensation product, H_4L, was not obtained at all. The presence of Mn^{2+} ions is essential to obtain the macrocyclic Schiff-base complexes, as reported for other systems.[3a,3b,9]

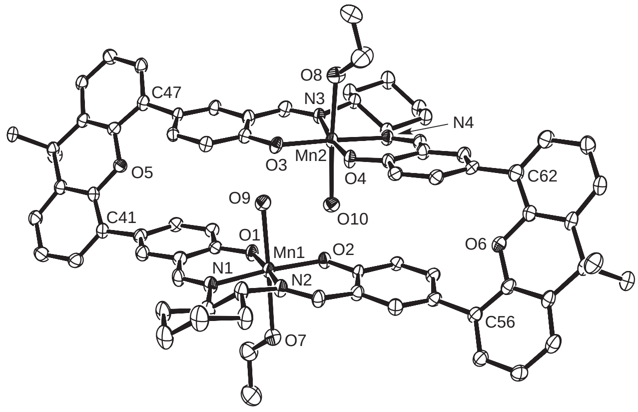


Figure 2. ORTEP drawing of the cationic part of **3** (thermal ellipsoids at the 50% probability level). Selected interatomic distances (Å): Mn1···Mn2, 5.0934(9); Mn1–O1, 1.885(3); Mn1–O2, 1.893(3); Mn1–O7, 2.289(3); Mn1–O9, 2.285(3); Mn1–N1, 1.998(4); Mn1–N2, 1.984(3); Mn2–O3, 1.904(3); Mn2–O4, 1.888(3); Mn2–O8, 2.252(3); Mn2–O10, 2.283(3); Mn2–N3, 1.998(3); Mn2–N4, 1.999(3).

The structure of **3** was confirmed by X-ray analysis (Figure 2).[8] Two manganese(III) Schiff-base units in the cationic dimanganese complex $[Mn_2(L)(EtOH)_2(H_2O)_2]^{2+}$ are connected by two 9,9-dimethylxanthene-4,5-diyl spacers to form a macrocyclic structure. Each manganese center is surrounded by N_2O_2 atoms from the Schiff-base ligand and two oxygen atoms of ethanol and water molecules at the axial positions. Complex **3** has a pseudo-C_2 axis through O5 and O6 atoms, thus the cofacial two manganese(III) Schiff-base units are aligned as an anti manner. The two manganese centers are separated by 5.0934(9) Å. In contrast to the parallel arrangement of two salicylaldehyde planes in **2**, the interplane separation demonstrated by the O1···O3 and O2···O4 distances [3.678(4) and 3.409(4) Å, respectively] is significantly smaller than the C41···C47 and C56···C62 distances [4.644(6) and 4.635(6) Å, respectively] in the xanthenediyl spacers. This difference is attributable to the two intramolecular O–H···O hydrogen bonds between the coordinated water oxygen and phenolato oxygen (O9···O3 = 2.865(4), O10···O2 = 2.873(4) Å).

A preliminary investigation of asymmetric oxidation of methyl phenyl sulfide by PhIO revealed that complex **3** and the corresponding mononuclear complex **4** catalyzed the reaction to give methyl phenyl sulfoxide in a moderate chemical yield (65% and 55%, respectively), but the enantioselectivity was extremely low (6% ee for **3** and **4**). Interestingly, addition of 4-(dimethylamino)pyridine to the reaction system improved the enantioselectivity to 22% ee in the case of **3**, but no effect for **4** (4% ee). The details of the catalytic reactions as well as further ligand designs based on **2** are under investigation.

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5 **1**$\cdot H_2O$: Anal. Calcd for $C_{15}H_{18}B_2O_6$: C, 57.03; H, 5.74%. Found: C, 57.00; H, 5.56%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.35 (s, 4H), 7.61 (m, 4H), 7.11 (t, $J = 7.5$ Hz, 2H), 1.57 (s, 6H). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 153.6, 134.4, 129.0, 128.7, 122.7, 120.6, 33.4, 32.4.

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7 **2**: Anal. Calcd for $C_{29}H_{22}O_5$: C, 77.32; H, 4.92%. Found: C, 77.08; H, 5.05%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.85 (s, 2H), 9.38 (s, 2H), 7.48–7.15 (m, 10H), 6.82 (d, $J = 8.4$ Hz, 2H), 1.74 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 195.5, 160.4, 147.2, 137.8, 135.1, 130.8, 129.2, 128.4, 128.1, 125.5, 123.4, 120.1, 117.2, 34.6, 32.2. Crystal Data: M_r 450.48, monoclinic, $P2_1/c$, $a = 8.668(2)$, $b = 19.732(2)$, $c = 13.264(2)$ Å, $\beta = 91.68(2)^\circ$, $V = 2267.6(7)$ Å^3, $Z = 4$, $D_c = 1.319$ g cm^{-3}, $T = 295$ K, R_1 $(I > 2.0\sigma(I)) = 0.060$, $wR_2 = 0.184$ (all data).

8 Anal. Calcd for **3**$\cdot$EtOH$\cdot H_2O$, $C_{76}H_{84}F_{12}Mn_2N_4O_{12}Sb_2$: C, 49.97; H, 4.63; N, 3.07%. Found: C, 50.28; H, 4.71; N, 3.17%. Crystal Data for **3**$\cdot$1.5EtOH$\cdot$2H_2O: fw 1867.93, monoclinic, $P2_1$, $a = 15.8627(7)$, $b = 13.0340(5)$, $c = 19.6598(9)$ Å, $\beta = 90.244(2)^\circ$, $V = 4064.7(3)$ Å^3, $Z = 2$, $D_c = 1.526$ g cm^{-3}, $T = 113$ K, R_1 $(I > 2.0\sigma(I)) = 0.051$, $wR_2 = 0.147$ (all data).

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