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Three Polyhydroxyl-Bridged Defective Dicubane Tetranuclear Mn^{III} Complexes: Synthesis, Crystal Structures, and Spectroscopic Properties

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Abstract: Three polyhydroxyl-bridged tetranuclear Mn^{III} complexes $[\text{Mn}_4(\text{L}^{1a})_2(\mu_3\text{-OMe})_2(\mu_2\text{-OMe})_2(\text{MeOH})_2]$ (**1**), $[\text{Mn}_4(\text{L}^{2a})_2(\mu_3\text{-OMe})_2(\mu_2\text{-OMe})_2(\text{H}_2\text{O})_2]$ (**2**), and $[\text{Mn}_4(\text{L}^{3a})_2(\mu_3\text{-OMe})_2(\mu_2\text{-OMe})_2(\text{H}_2\text{O})_2]$ (**3**) derived from $\text{Mn}^{\text{n+}}$ -promoted reactivity of Schiff base ligands ($\text{HL}^1 = 1\text{-}(4\text{-}[(\text{E})\text{-}3,5\text{-dichlorine-}2\text{-hydroxybenzylidene]amino)phenyl)ethanone O-benzyloxime}$, $\text{HL}^2 = 1\text{-}(4\text{-}[(\text{E})\text{-}3\text{-bromine-}5\text{-chloro-}2\text{-hydroxybenzylidene]amino)phenyl)ethanone O-benzyloxime}$, and $\text{HL}^3 = 1\text{-}(4\text{-}[(\text{E})\text{-}3,5\text{-dibromine-}2\text{-hydroxybenzylidene]amino)phenyl)ethanone O-benzyloxime}$) have been synthesized and characterized. In the Mn^{III} complexes **1**, **2**, and **3**, the newly formed ligands $(\text{L}^{1a})^{4-}$, $(\text{L}^{2a})^{4-}$, and $(\text{L}^{3a})^{4-}$ are derived from the chemoselective cleavage of the $\text{C}=\text{N}$ bond in the original Schiff base ligands HL^1 , HL^2 , and HL^3 to form corresponding halogenated salicylaldehyde, 3,5-dichlorosalicylaldehyde, 3-bromine-5-chlorosalicylaldehyde, and 3,5-dibrominesalicylaldehyde, respectively. Then, the further addition of acetone to two halogenated salicylaldehyde molecules in situ α,α double aldol reaction promoted by $\text{Mn}^{\text{n+}}$ ions in the presence of base to give the new ligands $(\text{L}^{\text{na}})^{4-}$. X-ray crystallographic analyses of the Mn^{III} complexes **1**, **2**, and **3** show that the three complexes are all tetranuclear structure and crystallizes in the triclinic system, space group $P\bar{1}$. The four Mn^{III} ions and bridging alkoxido groups are arranged in a face-shared dicubane-like core with two missing vertices. In the three Mn^{III} complexes, the asymmetric unit contains two kinds of different Mn^{III} ions (Mn1 and Mn2), where the Mn^{III} ions are all hexacoordinated with slightly distorted octahedral geometries. Simultaneously in the synthesis of multinuclear $\text{Mn}^{\text{n+}}$ complexes above, we explored the crystal structure, spatial configuration, and spectroscopic properties of the multinuclear Mn^{III} complexes with different halogen substituents.

Keywords: defective dicubane tetranuclear Mn^{III} complex; Schiff base ligand; manganese-promoted; double aldol addition; crystal structure; spectroscopic property

1. Introduction

There is a wide range of research space in aldol condensation reactions, in particular, in its asymmetric and catalytic field, via an asymmetric organic catalyst or chelating agent of the metal complex unit. Normally, the B, Ti, or Sn ions because of their specific Lewis acid properties are used for promoting enolization followed by aldol addition [1–3]. To a lesser extent, the other first row of transition metal Zr, Co, Ni, Cu, or Zn ions also have been used [4–6]. In addition, we have recently reported a tetranuclear Zn^{II} complex using a double aldol ligand formed in situ by α,α -double aldol addition of acetone to 3,5-dichlorosalicylaldehyde promoted by Zn^{II} ion in the presence of base [7]. In efforts to design new multidentate ligands which can form novel polynuclear complexes with attractive structural features, we are probing into this reaction using Lewis acid metal assistance. This

favorable reaction will allow to obtaining ligands that are extremely difficult to separate by classical anionic organic chemistry under conventional conditions. This, in turn, will allow the synthesis of novel-innovative metal complexes that are pre-restricted by ligand design [8–17]. Based on this, the transition metal Mn ion has become our target of choice due to its various oxidation states and Lewis acidity [18], which acts as a potential promoter to study the extent of the in situ aldol reaction of acetone and salicylaldehyde derivatives. Up to now, the use of Mn ions for the synthesis of aldol products has been relatively little explored, as reported, a unique one-pot α,α -double aldol addition of acetone to two o-vanillin molecules promoted by Mn^{n+} ions in situ, leading to a novel multidentate ligand, further obtained a rare defect-dicubane $\{\text{Mn}_4\}$ complex [19]. Therefore, we hope that we can synthesize a variety of multinuclear Mn complexes, explore the spatial structure and crystal parameters, and perhaps determine the laws.

Moreover Schiff base ligands and their complexes have been application in many fields [20–23], such as biological activity reagents [24–34], magnetic materials [35–43], luminescent materials [44–52]. Based on this, we designed and synthesized three Schiff base ligands with different halogen substituents and their Mn^{III} complexes **1**, **2**, and **3**, respectively. In the synthesis of this Mn^{III} complexes, due to the hydrolysis chemoselective cleavage of the C=N bond of the original Schiff base ligands (HL^1 , HL^2 , and HL^3), forms the corresponding halogenated salicylaldehyde molecules and further the α,α double aldol addition of acetone to two halogenated salicylaldehyde molecules promoted by Mn^{n+} ions in situ, leading to a unique corresponding multidentate polyhydroxyl ligand ($\text{L}^{\text{na}}\text{Mn}^{\text{III}}$) $^{4-}$, acetone-disalicylaldehyde aldol (Scheme 1). On the basis of the synthesis of multinuclear Mn^{III} complexes, we have investigated the crystal structure and spatial configuration of the multinuclear Mn^{III} complexes with different halogen substituents. To the best of our knowledge, a few aldol additions were previously reported as a one-pot reaction or a specific Mn^{n+} -promoted reaction.

Scheme 1. Synthesis of the multidentate polyhydroxyl ligand ($\text{L}^{\text{na}}\text{Mn}^{\text{III}}$) $^{4-}$ and their corresponding Mn^{III} complexes **1**, **2**, and **3**.

2. Experiments

2.1. Reagents and Physical Measurements

4-aminoacetophenone, O-benzylhydroxylamine and 3,5-dichlorosalicylaldehyde, 3-bromine-5-chlorosalicylaldehyde, and 3,5-dibrominesalicylaldehyde were purchased from Aldrich and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. C, H, and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer (Hanau, Germany). FT-IR spectra were recorded on a VERTEX70 FT-IR

spectrophotometer (Bruker, Karlsruhe, Germany), with samples prepared as KBr (500–4000 cm^{-1}). UV–vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer (Kyoto, Japan). X-ray single crystal structure was determined on a Bruker Smart Apex-II CCD diffractometer (Karlsruhe, Germany). ^1H NMR spectra were recorded using a Mercury-400BB spectrometer (Varian, Palo Alto, CA, USA) at 500 MHz. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company (Beijing, China) and the thermometer was uncorrected. Fluorescent spectra were performed on a LS-55 fluorescence photometer (Perkin-Elmer, Norwalk, CA, USA).

2.2. Synthesis of HL^1 , HL^2 , and HL^3

HL^1 , HL^2 , and HL^3 were synthesized according to an analogous method reported previously in the literature [53–60]. The synthetic route involved in the synthesis of HL^1 , HL^2 , and HL^3 are given in Scheme 2.

Scheme 2. Synthetic route of the ligands HL^1 , HL^2 , and HL^3 .

1-(4-Aminophenyl)ethanone O-benzyl oxime was synthesized according to an analogous method reported early [7]. To an ethanol solution (5 mL) of 1-(4-aminophenyl)ethanone (272.0 mg, 2.2 mmol) was added an ethanol solution (5 mL) of O-benzylhydroxylamine (270.0 mg, 2.2 mmol). The mixture solution was stirred at 328 K for 18 h. Cooled to room temperature, and the precipitate was filtered and washed successively with ethanol and n-hexane, respectively. The product was dried under vacuum and purified with recrystallization from ethanol to obtain 411.80 mg of 1-(4-aminophenyl)ethanone O-benzyl oxime. Yield, 85.2%. m.p. 352–353 K. Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}$ (%): C, 74.97; H, 6.71; N, 11.66; Found (%): C, 74.92; H, 6.76; N, 11.63. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ = 2.16 (s, 2H, CH_2), 2.52 (s, 3H, CH_3), 5.15 (s, 2H, Ar- NH_2), 6.84 (d, J = 8.1 Hz, 2H, Ar-H), 7.67–7.20 (m, 7H, Ar-H).

Add ({4-amino}phenyl)ethanone O-benzyl oxime (240.0 mg, 1.0 mmol) into ethanol solution (7 mL) of 3,5-dichlorosalicylaldehyde (191.5 mg, 1.0 mmol). The mixture solution was stirred at 333 K for 18 h. After cooling to room temperature, the precipitate was filtered and washed successively with ethanol and ethanol/n-hexane (1/4), respectively. The product was dried under reduced pressure to obtain 301.84 mg HL^1 , Yield, 79.2%. m.p. 402–403 K. Anal. Calcd. for Anal. Calcd. for $\text{C}_{22}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2$ (HL^1) (%): C, 63.93; H, 4.39; N, 6.78. Found (%): C, 63.99; H, 4.42; N, 6.75. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ = 2.25 (s, 3H, $-\text{CH}_3$), 5.23 (s, 2H, Ar- $\text{CH}_2\text{-O}$), 7.32–7.79 (m, 11H, Ar-H), 9.06 (s, 1H, $\text{CH}=\text{N}$), 14.35 (s, 1H, OH).

The ligands HL² and HL³ were prepared by a method similar to that of HL¹ except substituting 3,5-dichlorosalicylaldehyde with 3-bromine-5-chlorosalicylaldehyde or 3,5-dibrominesalicylaldehyde, respectively. HL²: 351.33 mg, Yield, 76.8%. m.p. 429–431 K. C₂₂H₁₈BrClN₂O₂ (HL²) (%): C, 57.73; H, 3.96; N, 6.12. Found: C, 58.04; H, 4.02; N, 6.08. ¹H NMR (500 MHz, DMSO-*d*₆) δ = 2.25 (s, 3H, –CH₃), 5.23 (s, 2H, Ar–NH₂), 7.32–7.87 (m, 11H, Ar–H), 9.04 (s, 1H, CH=N), 14.49 (s, 1H, OH). HL³: 419.84 mg, Yield, 83.8%. m.p. 441–442 K. C₂₂H₁₈Br₂N₂O₂ (HL³) (%): C, 52.62; H, 3.61; N, 5.58. Found: C, 52.71; H, 3.57; N, 5.75. ¹H NMR (500 MHz, DMSO-*d*₆) δ = 2.25 (s, 3H, –CH₃), 5.23 (s, 2H, Ar–CH₂–O), 7.32–7.93 (m, 11H, Ar–H), 9.08 (s, 1H, CH=N), 14.55 (s, 1H, OH).

2.3. Syntheses of Mn^{III} Complexes 1, 2, and 3

Complex 1: A solution of Mn(OAc)₂·4H₂O (2.5 mg, 0.01 mmol) in methanol (5 mL) was added dropwise to a solution of HL¹ (10.2 mg, 0.02 mmol) in acetone (3 mL) containing three drops of trimethylamine at room temperature. The color of the mixed solution turned red-brown immediately, then stirred for 0.5 h at room temperature. The mixture solution was filtered and the filtrate was allowed to stand at room temperature for about two weeks. The solvent was partially evaporated and obtained several red-brown prismatic single crystals suitable for X-ray crystallographic analysis. The yield was 52% (based on the total available Mn). Anal. Calcd. for C₄₀H₄₀Cl₈Mn₄O₁₆ (%): C, 37.53; H, 3.15. Found: C, 37.59; H, 3.21.

Complex 2: Complex 2 and 3 were synthesized by adding a solution of Mn(OAc)₂·4H₂O (2.5 mg, 0.01 mmol) in methanol (5 mL) dropwise to HL² (10.3 mg, 0.02 mmol) in acetone (3 mL), HL³ (10.4 mg, 0.02 mmol) in acetone (3 mL), respectively, and others steps are same as complex 1. The yields were 56% and 59% (based on the total available Mn), respectively. **Complex 2:** C₃₈H₃₆Cl₄Br₄Mn₄O₁₆ (%): C, 31.92; H, 2.54. Found: C, 32.17; H, 2.38. **Complex 3:** C₃₈H₃₆Br₈Mn₄O₁₆ (%): C, 28.39; H, 2.26. Found: C, 28.37; H, 2.28.

2.4. X-Ray Crystallography

The selected single crystals of complexes 1, 2, and 3 were put in a sealed tube, and the measurement was performed on a Bruker Smart Apex-II CCD diffractometer (Karlsruhe, Germany). The reflections were collected by a graphite monochromated Cu K α radiation (λ = 1.54184 Å) at 293(2) K and 296.15(2) K for Mn^{III} complexes 1 and 3, respectively, and that of 2 was collected by a graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 296.15(2) K. The SMART and SAINT software packages [61] were used for data collection and reduction respectively. Absorption corrections based on multiscans using the SADABS software [62] were applied. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 using the SHELXL program [63]. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and isotropically fixed in the final refinement. Details of the crystal parameters, data collection, and refinements for complexes 1, 2, and 3 are summarized in Table 1. Supplementary crystallographic data for this paper have been deposited at the Cambridge Crystallographic Data Centre (1538187, 1538179, and 1538146 for complexes 1, 2, and 3) and can be gained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

Table 1. Crystal data and structure refinement for Mn^{III} complexes **1**, **2**, and **3**.

Compound	1	2	3
Empirical formula	C ₄₀ H ₄₀ Cl ₈ Mn ₄ O ₁₆	C ₃₈ H ₃₆ Br ₄ Cl ₄ Mn ₄ O ₁₆	C ₃₈ H ₃₆ Br ₈ Mn ₄ O ₁₆
Formula weight	1280.08	1429.87	1607.71
Temperature/K	293(2)	296.15	296.15
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	9.3045(13)	9.4483(15)	9.3658(5)
<i>b</i> /Å	11.792(3)	11.392(2)	11.2509(7)
<i>c</i> /Å	12.408(3)	12.650(4)	12.7732(7)
α /°	70.12(2)	72.261(6)	72.341(4)
β /°	75.412(16)	75.408(6)	76.598(4)
γ /°	80.928(15)	81.766(6)	81.729(4)
Volume/Å ³	1235.1(5)	1251.7(5)	1243.68(13)
<i>Z</i>	1	1	1
ρ_{calc} g/cm ³	1.721	1.897	2.147
μ /mm ^{−1}	12.696	4.456	16.170
<i>F</i> (000)	644.0	700.0	774.0
Crystal size/mm ³	0.28 × 0.26 × 0.24	0.26 × 0.25 × 0.24	0.28 × 0.25 × 0.22
Radiation	Cu <i>K</i> α (λ = 1.54184)	Mo <i>K</i> α (λ = 0.71073)	Cu <i>K</i> α (λ = 1.5418)
2 θ range/°	7.756 to 131.996	3.764 to 50.016	7.412 to 131.958
Index ranges	−10 ≤ <i>h</i> ≤ 5, −13 ≤ <i>k</i> ≤ 13, −14 ≤ <i>l</i> ≤ 14	−8 ≤ <i>h</i> ≤ 11, −13 ≤ <i>k</i> ≤ 13, −15 ≤ <i>l</i> ≤ 15	−9 ≤ <i>h</i> ≤ 10, −13 ≤ <i>k</i> ≤ 13, −14 ≤ <i>l</i> ≤ 15
Reflections collected	7361	7494	8978
Independent reflections	4258 [<i>R</i> _{int} = 0.0927, <i>R</i> _{sigma} = 0.1358]	4201 [<i>R</i> _{int} = 0.0532, <i>R</i> _{sigma} = 0.0759]	4135 [<i>R</i> _{int} = 0.0386, <i>R</i> _{sigma} = 0.0485]
Data/restraints/parameters	4258/3/314	4201/0/301	4135/0/301
Goodness-of-fit on <i>F</i> ²	1.077	1.023	1.101
<i>R</i> (<i>I</i> ≥ 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0765, <i>wR</i> ₂ = 0.1792	<i>R</i> ₁ = 0.0904, <i>wR</i> ₂ = 0.2548	<i>R</i> ₁ = 0.0627, <i>wR</i> ₂ = 0.1871
<i>R</i> (all data)	<i>R</i> ₁ = 0.1275, <i>wR</i> ₂ = 0.2256	<i>R</i> ₁ = 0.1329, <i>wR</i> ₂ = 0.2905	<i>R</i> ₁ = 0.0743, <i>wR</i> ₂ = 0.1979
Largest diff. peak/hole/eÅ ^{−3}	0.571/−1.079	1.011/−0.840	1.23/−0.81

3. Results and Discussion

3.1. Synthesis

Synthesis of Mn^{III} complexes **1**, **2**, and **3** consisting of the addition of Schiff base ligands (HL¹, HL², and HL³) to the acetone solution containing a small amount of triethylamine, respectively, followed by addition of a solution of Mn(OAc)₂·4H₂O in methanol (5 mL). It is worth noticing that the C=N bond of the original Schiff base ligands HL¹, HL², and HL³ have chemoselectively cleaved due to the hydrolytic action and gave the corresponding halogenated salicylaldehyde derivatives, 3,5-dichlorosalicylaldehyde, 3-bromine-5-chlorosalicylaldehyde, and 3,5-dibrominesalicylaldehyde, respectively. Then a unique one-pot α,α double aldol addition in situ of acetone to two corresponding halogenated salicylaldehyde molecules promoted by Mnⁿ⁺ ions, resulting to the corresponding new multidentate ligands H₄L^{1a}, H₄L^{2a}, and H₄L^{3a}, acetone-disalicylaldehyd aldol (Scheme 1), respectively. In the process of synthesis of Mn^{III} complexes **1**, **2**, and **3**, triethylamine acts as a base in this reaction forming bridging oxides, methoxides, and ligands after deprotonation.

It is worth noting that, in order to explore the oxidation of manganese ions, the same reactions to synthesis the Mn^{III} complexes **1**, **2**, and **3** were carried out under air-free conditions to prevent the oxidation of Mn^{II} to Mn^{III}. As well as the reaction were carried out under acetone-free and Mn salt-free conditions (see Supporting Information). However, these reactions did not give any crystals of the complex product nor any aldol product in the solution (analyzed by NMR), which leads us to believe that Mn^{III} is more likely to promote the α,α double aldol addition, and the acetone is also a necessary factor.

Based on the above findings, our proposed mechanism to rationalize the formation of the new generated polyhydroxyl multidentate ligands, H_4L^{1a} , H_4L^{2a} , and H_4L^{3a} , by Mn^{n+} -promoted α,α -double aldol additions [7,19] is described in Scheme 3. Firstly, the initial Schiff base ligands (HL^1 , HL^2 , and HL^3) underwent hydrolysis to get 1-(4-aminophenyl)ethanone O-benzyl oxime and corresponding salicylaldehyde derivatives (3,5-dichlorosalicylaldehyde, 3-bromine-5-chlorosalicylaldehyde, 3,5-dibrominesalicylaldehyde), respectively (Scheme 3A). Then, a molecule of acetone is deprotonated by the hydroxide moiety of the base, triethylamine, yielding enolate *i*, which is stabilized by the keto-enolate mesomeric effect as well as coordination to Mn^{n+} (Scheme 3B). Moreover, the phenol position of salicylaldehyde derivatives is also deprotonated by the hydroxide base leading to a Mn^{n+} -phenolate complex *ii*. The concomitant coordination of the Mn^{n+} ion to the neighboring carbonyl oxygen atom of salicylaldehyde derivatives allows the activation of the aldehyde function which undergoes the first aldol addition of the acetone enolate *i*, yielding the first aldol product *iii* (Scheme 3C). The latter can then be further deprotonated either in the α or α' position from the carbonyl of the acetone residue. Deprotonation of *iii* occurs predominantly in the α position due to the thermodynamic conditions used which favor deprotonation on the most substituted α position (Scheme 3D). The formation of enolate *iv*, stabilized by the keto-enolate mesomeric effect, is also promoted by Mn^{n+} coordination assistance. Enolate *iv* can undergo another aldol addition on a second molecule of salicylaldehyde derivatives, activated by its coordination to Mn^{n+} , leading to the ligand acetone-di-salicylaldehyde aldol *v* (H_4L^{1a} , H_4L^{2a} and H_4L^{3a}) which is quadruply deprotonated and coordinated to two Mn^{n+} ions.

3.2. IR Spectra

The FT-IR spectra of Mn^{III} complexes **1**, **2**, and **3** exhibit various bands in the 500–4000 cm^{-1} region. The most important FT-IR bands are listed in Table 2. In the Mn^{III} complexes **1**, **2**, and **3**, the bands appear at about 3437, 3416, and 3445 cm^{-1} , respectively, are attribute to O–H stretching frequency coordination methanol or water molecules, which confirmed by the crystal structure [64–69]. No characteristic C=N stretching band is found in complexes **1**, **2**, and **3** indicating that the ligands HL^1 , HL^2 , and HL^3 are converted into the polyhydroxy deprotonation ligands and coordinated to the Mn^{III} ions. The frequency of Ar–O and C–O stretching vibration shows a strong band at 1244 and 1156 cm^{-1} , 1296 and 1167 cm^{-1} , and 1275 and 1173 cm^{-1} in the Mn^{III} complexes **1**, **2**, and **3**, respectively [70–73]. The characteristic stretching of the carbonyl (C=O) group appears at 1587, 1602, and 1620 cm^{-1} as the strong bands in the Mn^{III} complexes **1**, **2**, and **3**, respectively. The moderate and weak vibrations appearing around 698 and 503 cm^{-1} in **1** (698 and 503 cm^{-1} in **2**, 698 and 503 cm^{-1} in **3**) correspond to the asymmetric and symmetric stretching vibrations of the Mn–O–Mn, respectively, indicating that the Mn–O bond forms at the Mn^{III} ions and the oxygen atoms.

Table 2. Selected FT-IR data for Mn^{III} complexes **1**, **2**, and **3** (cm^{-1}).

Complex	$\nu(O-H)$	$\nu(Ar-O, C-O)$	$\nu(C=O)$	$\nu(Mn-O)$	$\nu(C=C)$ Benzene Ring Skeleton
1	3437	1244, 1155	1587	698, 503	1449, 1412
2	3416	1296, 1167	1602	695, 494	1449, 1352
3	3445	1275, 1173	1620	694, 471	1476, 1368

Scheme 3. Proposed mechanism for the Mn^{n+} -promoted α,α double aldol additions. (A) Hydrolysis of Ligands HL¹, HL², and HL³. (B) Deprotonation of the acetone. (C) Activation of the salicylaldehyde derivatives and aldol addition. (D) Deprotonation of the aldol product and second aldol addition.

3.3. UV-vis Absorption Spectra

The UV-vis spectra of the Mn^{III} complexes **1**, **2**, and **3** were recorded in 1.0×10^{-5} mol·L⁻¹ DMF solution at room temperature shown in Figure 1.

Figure 1. UV-vis absorption spectra of the Mn^{III} complexes **1**, **2**, and **3** in DMF solution ($c = 1 \times 10^{-5}$ mol/L).

A broad absorption band at 443, 417, and 410 nm in complexes **1**, **2**, and **3** are observed, respectively, which can be attributed to the L→M charge-transfer transitions. In the complex **2**, the peak at 297 can be assigned to the n→π* charge transition of the C=O bond of the new ligand (L^{2a})⁴⁻ unit, probably arising from the charge transfer of an oxygen atom in the methoxy group to the Mn^{III} center. The shoulder band at 472 nm can attribute to the d-d transitions for elongated octahedral Mn^{III} ions [74–77], however, which are not observed in complexes **1** and **3** maybe because of the weaker d-d transitions absorption peak of Mn^{III} ions are obscured by the stronger L→M charge-transfer absorption peak of the complexes.

3.4. Crystal Structure of Mn^{III} Complexes **1**, **2**, and **3**

Crystal structures and atom numberings of complexes **1**, **2**, and **3** are depicted in Figures 2–4, respectively. Selected bond lengths and angles for the Mn^{III} complexes **1**, **2**, and **3** are listed in Table S1. X-ray crystal structure analyses revealed that the Mn^{III} complexes **1**, **2**, and **3** take on similar crystal structures, which all are centrosymmetric tetranuclear cluster. The crystals of Mn^{III} complexes are all solved as triclinic space group *P*-1. All the Mn^{III} complexes **1**, **2**, and **3** consist of four Mn^{III} ions, two (L^{na})⁴⁻ ($n = 1$ (**1**), $n = 2$ (**2**), $n = 3$ (**3**)) moieties, two μ₃-OMe and two μ₂-OMe units, two coordinated methanol molecules (in **1**) or water molecules (in **2** and **3**) (Figure 2a). The Mn^{III} ions and bridging alkoxido groups are arranged in a face-shared dicubane-like core with two missing vertices, which is typical Mn₄ “defect-dicubane” structure known [78]. The planar Mn₄ rhombus can be described as being composed of two Mn₃ triangular faces, each held together by a μ₃-oxygen atom [O6 or O6a ($a = 1 - x, 1 - y, 1 - z$)] of a CH₃O⁻ ligand with distances to the Mn^{III} atoms in the range 2.004(5)–2.265(5) Å in **1** (1.996(6)–2.272(6) Å in **2**, 2.009(4)–2.256(4) Å in **3**), which are nearly equal to that in the similar complexes [Mn^{III}₄(AcVn₂)₂(μ₃-OMe)₂(μ-OMe)₂(MeOH)₂] [19]. The Mn2–O6–Mn1, Mn2–O6–Mn1a, and Mn1–O6–Mn1a ($a = 1 - x, 1 - y, 1 - z$) angles are 101.4(2)°, 93.9(2)°, and 99.1(2)° in **1**, respectively (101.4(3), 93.3(3)°, and 100.4(3)° in **2**; 101.1(2)°, 93.4(2)°, and 100.3(2)° in **3**). The two

Mn^{III} (Mn1 and Mn1a ($a = 1 - x, 1 - y, 1 - z$)) ions lie on the common edge of the two triangular faces. The external edges of each triangle are held by μ_2 -oxygen atoms (O2, O2a ($a = 1 - x, 1 - y, 1 - z$)) and (O7, O7a ($a = 1 - x, 1 - y, 1 - z$)) with distances of 1.866(6) and 2.226(5) Å of O2 to Mn1 and Mn2 in **1** (1.863(6) and 2.210(6) Å in **2**, 1.863(4) and 2.227(4) Å in **3**) as well as 1.922(6) and 1.968(6) Å of O7 to Mn1 and Mn2 in **1** (1.904(6) and 1.967(6) Å in **2**, 1.918(4) and 1.966(5) Å in **3**), respectively (Figure 2b), which are similar to the complexes of Schiff base ligands previously reported [79]. The Mn1–O2–Mn2 and Mn1–O7–Mn2a ($a = 1 - x, 1 - y, 1 - z$) angle is 99.5(2)° and 108.1(2)° in **1** (99.8(3)° and 108.3(3)° in **2**, 99.6(2)° and 107.6(2)° in **3**), respectively.

Figure 2. (a) Molecule structure and atom numbering of complex **1** (hydrogen atoms are omitted for clarity); (b) the planar Mn₄ rhombus and (c) the coordination polyhedra for Mn^{III} atoms of complex **1** (symmetry code: $a = 1 - x, 1 - y, 1 - z$).

Figure 3. (a) Molecule structure and atom numbering of complex 2 (hydrogen atoms are omitted for clarity); (b) the planar Mn₄ rhombus and (c) the coordination polyhedra for Mn^{III} atoms of complex 2 (symmetry code: $a = 1 - x, 1 - y, 1 - z$).

Figure 4. (a) Molecule structure and atom numbering of complex 3 (hydrogen atoms are omitted for clarity); (b) the planar Mn₄ rhombus and (c) the coordination polyhedra for Mn^{III} atoms of complex 3 (symmetry code: $a = 1 - x, 1 - y, 1 - z$).

In the crystal structures of Mn^{III} complexes **1**, **2**, and **3**, the asymmetric unit contains two kinds of different Mn^{III} ions, the metal center Mn1 is hexa-coordinated by three O (O7, O6, O6a ($a = 1 - x, 1 - y, 1 - z$)) atoms from one μ_2 -OMe and two μ_3 -OMe units, respectively, and the remaining three O atoms (O1, O2, and O5) are from a multidentate polyhydroxyl (L^{na})^{4−} ligands. The coordination geometry of Mn1 can be described as a slightly distorted octahedron geometry based on the corresponding bond lengths and angles (Figure 2c). The equatorial donor atoms O1, O2, O6, and O7 are nearly co-planar, with slight deviation from the mean plane: 0.050(2), −0.053(1), 0.051(2), and −0.048(3) Å in **1** (0.051(3), −0.054(2), 0.052(2), and −0.050(1) Å in **2**, 0.050(2), −0.053(4), 0.050(2), and −0.048(3) Å in **3**), respectively, and the Mn1 atom deviates by only 0.091(2) Å in **1** (0.095(3) Å in **2**, 0.093(1) Å in **3**) from this plane. As expected for the Mn^{III} ion, the axial Mn1–O5 and Mn1–O6a ($a = 1 - x, 1 - y, 1 - z$) distances of 2.194(6) Å and 2.265(5) Å in **1** (2.210(7) Å and 2.272(6) Å in **2**, 2.208(5) Å and 2.256(4) Å in **3**), respectively, are longer than the four Mn–O distances in equatorial sites with Mn1–O1 = 1.899(6) Å, Mn1–O2 = 1.866(6) Å, Mn1–O6 = 2.005(5) Å, Mn1–O7 = 1.922(6) Å in **1** (Mn1–O1 = 1.882(7) Å, Mn1–O2 = 1.863(6) Å, Mn1–O6 = 1.996(6) Å, Mn1–O7 = 1.904(6) Å in **2** and Mn1–O1 = 1.885(5) Å, Mn1–O2 = 1.863(4) Å, Mn1–O6 = 2.008(4) Å, Mn1–O7 = 1.918(4) Å in **3**). Obvious bond elongation, due to Jahn–Teller effect, is observed for the apical bonds O5–Mn1–O6a, which is expected for high-spin Mn^{III} as well as on the basis of charge considerations. This phenomenon is often found in the Mn^{III} complexes [80]. The Mn2 atoms are also hexa-coordinated by one O atom (O8) of solvent methanol (in **1**) or water molecule (in **2** and **3**), two O atoms (O7, O6) from μ_2 -OMe and μ_3 -OMe units, respectively, and the remaining three O atoms (O2, O3, O4) come from the (L^{na})^{4−} ligands, which generate an elongated octahedron around Mn2 on the basis of the corresponding bond lengths and angles (Figure 2c). The square bases of the octahedron for Mn2 consist of O3, O4, O6, O7a ($a = 1 - x, 1 - y, 1 - z$), with the apical position occupied by O2 and O8. Similarly, the apical bonds along O2–Mn2–O8 direction are elongated. The Mn···Mn separations are 3.253(2) Å for Mn1···Mn1a ($a = 1 - x, 1 - y, 1 - z$), 3.133(2) Å for Mn1···Mn2a, 3.149(2) Å for Mn1···Mn2a ($a = 1 - x, 1 - y, 1 - z$), and 5.374(2) Å for Mn2···Mn2a ($a = 1 - x, 1 - y, 1 - z$) in **1** (that of 3.282(2) Å, 3.123(3) Å, 3.138(2) Å and 5.332(2) Å in **2**, 3.277(1) Å, 3.133(1) Å, 3.135(1) Å and 5.343(1) Å in **3**). This phenomenon is consistent with the literature report [19,81,82].

The molecular structures of Mn^{III} complexes **1**, **2**, and **3** are similar to each other, but because of the intra- and inter-molecular hydrogen bond interactions (Table 3), their supramolecular structures are different. As illustrated in Figure 5, in the Mn^{III} complex **1**, there are three pairs of intramolecular (O8a–H8A···O1, C18–H18B···O7 and C19a–H19C···O4 ($a = 1 - x, 1 - y, 1 - z$)) hydrogen bond interactions which are helpful to stabilize the whole architecture. Furthermore, the complex **1** molecules interlinks into one 1D infinite chains along the *a* axis by a pair of weak intermolecular C19b–H19Ab···O5 ($b = 2 - x, 1 - y, 1 - z$) hydrogen bond interactions and the other 1D infinite chains [83,84] along the *b* axis by a pair of C11c–H11c···O3 ($c = 1 - x, 2 - y, 1 - z$) hydrogen bond interactions, respectively (Figures 6 and 7). Thus, these two 1D chains interlink to each other resulting to the crystal packing of the Mn^{III} complex **1** shown a 2D-layer supramolecular structure [85–89] parallel to the *ab*-planes (Figure 8).

Table 3. Main hydrogen bonds [$\text{\AA},^\circ$] for Mn^{III} complexes **1**, **2**, and **3**.

Compound	D–H...A	d(D–H)	d(H...A)	d(D...A)	∠D–H...A
1	O8A–H8A...O1	0.85	2.01	2.767(1)	149
	C18–H18B...O7	0.96	2.59	3.159(1)	118
	C19–H19C...O4	0.96	2.65	2.992(1)	115
	C11–H11...O3	0.98	2.57	3.470(1)	153
	C19–H19A...O5	0.96	2.60	3.406(1)	142
2	O8–H8B...O1	0.85	2.06	2.830(1)	150
	C18–H18A...O7	0.96	2.58	3.128(1)	116
	C19–H19B...O4	0.96	2.40	2.954(2)	116
	C11–H11...O3	0.98	2.38	3.286(1)	154
3	C19–H19B...O4	0.96	2.45	2.991(1)	115
	C11–H11...O3	0.98	2.28	3.182(8)	152

Figure 5. Part of intramolecular C–H...O hydrogen-bonding interactions in Mn^{III} complex **1** (symmetry code: a = 1 – x, 1 – y, 1 – z).

Figure 6. Part of 1D supramolecular structure containing C19b–H19Ab...O5 hydrogen bond interactions along *a* axis of the Mn^{III} complex **1** (symmetry code: b = 2 – *x*, 1 – *y*, 1 – *z*).

Figure 7. Part of 1D supramolecular structure containing C11c–H11c $\cdots$ O3 hydrogen bond interactions along *b* axis of the Mn^{III} complex **1** (symmetry codes: $c = 1 - x, 2 - y, 1 - z$).

Figure 8. View of the 2D layered motif within Mn^{III} complex **1** (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

In complex **2**, three pairs of intra-molecular O8–H8B $\cdots$ O1, C18–H18A $\cdots$ O7, and C19a–H19Ba $\cdots$ O4 ($a = 1 - x, 1 - y, 1 - z$) hydrogen bonds are formed (Figure 9), which are helpful to stabilize the whole architecture. The –O8H8B of coordinated water is hydrogen-bonded to the O1 atom of the (L^{2a})^{4–} ligand. The proton (–C18H18A) of the μ_3 -MeO[–] units is hydrogen-bonded to the O7 atom of the μ_2 -MeO[–] units. The proton (–C19aH19Ba ($a = 1 - x, 1 - y, 1 - z$)) of the μ_2 -MeO[–] units is hydrogen-bonded to the O4 atom of the (L^{2a})^{4–} ligand. Synchronously, the independent complexes are held together from zero-dimension into 1D supramolecular chains along the crystallographic *b* axis through a pair of intermolecular C11c–H11c $\cdots$ O3 ($c = 1 - x, 2 - y, 1 - z$) hydrogen bonding (Figure 10).

Figure 9. Part of intramolecular C–H...O hydrogen-bonding interactions in Mn^{III} complex **2** (symmetry codes: a = 1 – x, 1 – y, 1 – z).

Figure 10. 1D supramolecular structure containing C11c–H11c...O3 hydrogen bond interactions in complex **2** along *b* axis (symmetry codes: c = 1 – *x*, 2 – *y*, 1 – *z*).

In the crystal structure of complex **3**, there are a pair of intramolecular hydrogen bonds C19a–H19Ba...O4 ($a = 1 - x, 1 - y, 1 - z$) to stabilize the whole architecture (Figure 11, Table 3). Meanwhile, the complex **3** interlinks into one 1D infinite chain along the *b* axis by a weak intermolecular C11c–H11c...O3 ($c = 1 - x, 2 - y, 1 - z$) hydrogen bond interaction [90–93] (Figure 12).

Figure 11. Part of intramolecular C–H...O hydrogen-bonding interactions in Mn^{III} complex **3** (symmetry codes: $a = 1 - x, 1 - y, 1 - z$).

Figure 12. Part of 1D supramolecular structure containing C11c–H11c...O3 hydrogen bond interactions along the b axis in complex **3** (symmetry codes: $c = 1 - x, 2 - y, 1 - z$).

3.5. Fluorescence Properties

The emission spectra of the Mn(III) complexes **1**, **2**, and **3** were investigated in dilute DMF solution (5.0×10^{-5} mol/L) at room temperature (Figure 13). The complexes exhibit the bluish violet photoluminescence with maximum emissions at 486, 494, and 501 nm (π - π^*) upon excitation at 320 nm. The changes of the maximum emission wavelength and fluorescence intensity may be related to the different substituents on complexes **1**, **2**, and **3** [94–100]. As discussed above, because of the coordination of Mn^{III} ions to the ligand, which resulting in increasing of the delocalization of electrons and reducing the energy gaps between the π - π^* molecular orbitals of the ligand in the complexes (from **3**, **1** to **2**).

Figure 13. Emission spectra of the Mn^{III} complexes **1**, **2** and **3** ($\lambda_{\text{ex}} = 320 \text{ nm}$) in DMF solution ($5.0 \times 10^{-5} \text{ mol/L}$).

4. Conclusions

Based on the above data, description and discussion, three tetranuclear Mn^{III} complexes with defective double-cubane cores, namely $[\text{Mn}_4(\text{L}^{1a})_2(\mu_3\text{-OMe})_2(\mu_2\text{-OMe})_2(\text{MeOH})_2]$ (**1**), $[\text{Mn}_4(\text{L}^{2a})_2(\mu_3\text{-OMe})_2(\mu_2\text{-OMe})_2(\text{H}_2\text{O})_2]$ (**2**), and $[\text{Mn}_4(\text{L}^{3a})_2(\mu_3\text{-OMe})_2(\mu_2\text{-OMe})_2(\text{H}_2\text{O})_2]$ (**3**) have been synthesized and characterized. X-ray crystal structure determinations revealed that the structural features of complexes **1**, **2**, and **3** are similar except for the differences in the coordinated solvent molecules and the substituent of the ligands. There are worth noting that when the Schiff base ligand reacted with Mn^{III} acetate tetrahydrate, they undergo an one-pot chemoselective cleavage of the $\text{C}=\text{N}$ bond and further the α,α double aldol addition of acetone to two salicylaldehyde derivatives molecules promoted by $\text{Mn}^{\text{n+}}$ ions in situ, leading to the novel multidentate polyhydroxyl ligand $(\text{L}^{1a})^{4-}$, $(\text{L}^{2a})^{4-}$, and $(\text{L}^{3a})^{4-}$. This has proved an effective route to obtain the multidentate ligands and their tetranuclear Mn^{III} compounds. In these Mn^{III} complexes, all hexa-coordinated Mn^{III} atoms adopt elongated slightly distorted octahedral geometries. In addition, the Mn^{III} complex **1** possess a self-assembling infinite 2D supramolecular structure, whereas complexes **2** and **3** show the 1D chain. Interestingly, the existence of substituent effect in complexes **1**, **2**, and **3** may be responsible for the slight differences in their coordination geometries, supramolecular structure, and fluorescence properties.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/8/7/272/s1>, Table S1: Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) for Mn^{III} complexes **1**, **2** and **3**.

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