Letter

First synthesis and crystal structure of a Mn^{3+} complex derived from the Ogawa porphyrin-like ligand

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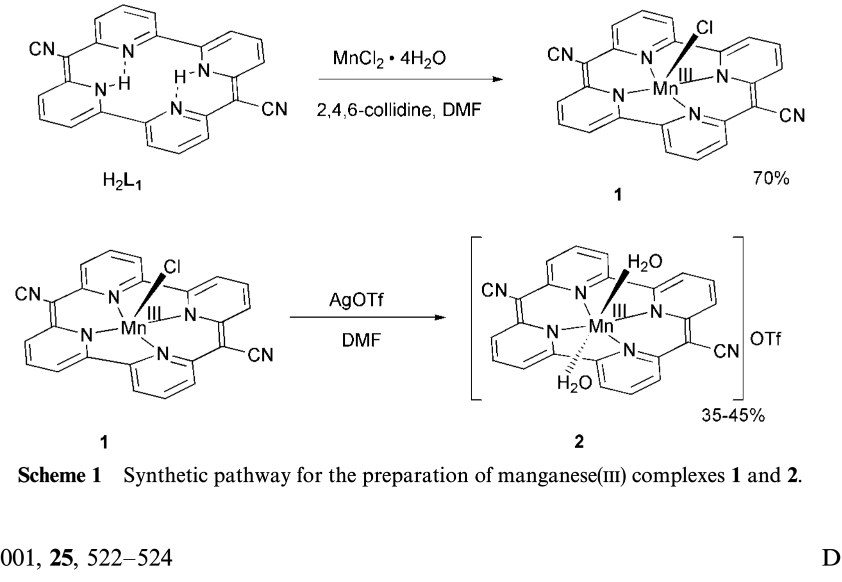
The synthesis and X-ray structure analysis of a new manganese(III) complex $[MnL_1(H_2O)_2]OTf$ displaying structural analogies with metalloporphyrins are described. This compound is characterized by very short Mn–N bond distances (1.93 Å) and a nearly planar structure. Its ability to catalyze cyclohexene epoxidation in the presence of MCPBA has also been evaluated.

Synthetic metalloporphyrins have found use in numerous applications, including the catalytic oxidation of organic substrates[1] and the fabrication of novel materials.[2] In light of the general importance of these compounds, the syntheses and metal coordination chemistry of porphyrin analogs have been attracting considerable interest. Porphyrin analogs are macrocyclic ligands that contain four or more pyrroles and some degree of conjugation, of which phthalocyanines, corroles, sapphirin, porphycene and calix[4]pyrroles are representative examples.[3] Twenty years ago, Ogawa and co-workers described the synthesis of a highly conjugated macrocycle presented as a porphyrin analog, by coupling two bipyridine units with acetonitrile.[4] Surprisingly, although this ligand is very reminiscent of porphyrins in terms of ring conjugation, planarity and charge, as well as core cavity size, no transition metal complexes have been reported so far. We then wondered if this interesting macrocyclic ligand would be appropriate for transition metal complexation, and thus could enlarge its scope of application. In this paper we wish to describe the synthesis and the structural characterization of new manganese(III) porphyrin-related complexes, as well as preliminary alkene epoxidation experiments.

The ligand H_2L_1 was synthesized in one step starting from 2,6-dibromopyridine, according to the procedure described by Ogawa and coworkers (yield 15%). The manganese complex $[Mn^{III}L_1Cl]$ (**1**) was obtained using the conventional method for manganese(III) porphyrin preparation by heating a DMF solution of H_2L_1 and $MnCl_2 \cdot 4H_2O$ at 140 °C for 6 h in the presence of 2,4,6-collidine (Scheme 1). Concentration of the solution and subsequent cooling to 4 °C afforded complex **1** as a black–grey powder (yield 70%).

In order to increase the solubility of the $[Mn^{III}L_1Cl]$ complex in acetonitrile and methanol, we performed a ligand exchange by stirring **1** in the presence of an excess of silver(I) triflate (AgOTf) in DMF at room temperature for 48 h. Evaporation of the DMF solution to dryness under reduced pressure and crystallization from methanol gave the $[Mn^{III}L_1(H_2O)_2]OTf$ complex **2** in 35–45% yield. LSIMS mass spectra of complexes **1** and **2** gave a parent peak with $m/z = 439$ (100%; L_1Mn^+), whatever the axial ligand.

Crystals of **2** suitable for X-ray diffraction studies were obtained by slow recrystallization at 4 °C from a methanolic solution. A representation of the structure, in which the hydrogen atoms and the counter anion have been omitted, is presented in Fig. 1. Despite the low diffracting quality of the crystal studied, valuable structural information can be



Scheme 1 Synthetic pathway for the preparation of manganese(III) complexes **1** and **2**.

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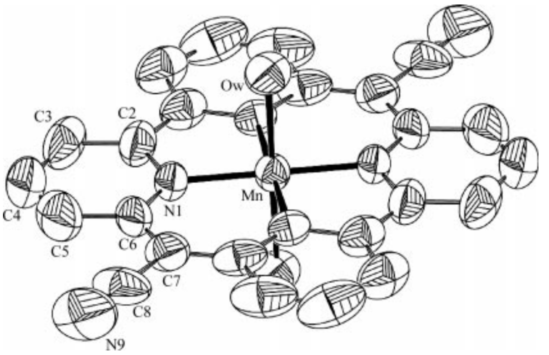

Fig. 1 An ORTEP drawing of the $[MnL_1(H_2O)_2]^+$ cation showing the coordination environment of the octahedral Mn(III) center. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Mn–N1 1.928(8), Mn–Ow 2.26(1), N1–C2 1.40(1), C2–C3 1.39(2), C3–C4 1.40(2), C4–C5 1.32(2), C5–C6 1.42(2), C6–N1 1.34(1), C6–C7 1.41(2), C7–C8 1.41(3), C8–N9 1.15(2), N1–Mn–N1′ 85.5(6), N1–Mn–N1″ 94.5(6), N1–Mn–Ow 89.8(3), N1–Mn–Ow′ 90.2(3), Ow–Mn–Ow′ 180.0.

obtained. In the solid state, the cyano groups do not participate in the coordination between neighboring cations. The manganese atom lies in a slightly elongated octahedral environment with two aqua molecules as axial ligands, the metal lying perfectly in the plane determined by the four nitrogen atoms. The O–Mn–O axis is nearly perpendicular to this plane, the octahedron being elongated along this axis. The Mn–N distances in this complex (1.93 Å) are significantly shorter than those usually observed for Mn(III) phthalocyanines (1.96 Å) or porphyrins (2.01 Å).[5] This is due to the smaller complexing cavity of ligand H_2L_1, which has two atoms less than the porphyrins in the complexing ring. Distortions from orthogonality are observed within the N–Mn–N bite angles owing to the constraints imposed by the five- and six-membered chelating rings. The Mn–Ow bond length is in the range expected for this bond in similar compounds [2.22 Å for Mn(III)TMPyP]. In the solid state the water molecule interacts with the triflate (OTf) counter anion through H-bonding (not shown). The Ow–O distance (2.99 Å) and the Ow–O–S angle (117°) are in agreement with such an interaction.

The temperature dependence of the magnetic susceptibility for complex **1** is in agreement with a high-spin ($S = 2$) manganese(III) atom.

UV-visible spectra were recorded in DMF. A λ_{max} value at 383 nm ($\varepsilon = 21\,600\ M^{-1}\ cm^{-1}$) was measured for **2**. This ε value is significantly lower than those observed for Mn(III) porphyrins: this is due to the smaller number of delocalized π-electrons.

The general structural features of complexes **1** and **2** are very reminiscent of their porphyrin parents in terms of geometry and physical properties. The complexation unit possesses four nitrogen atoms arranged in a cyclic manner; two nitrogen atoms are deprotonated thus affording a doubly negatively charged ligand. The ligand, as in porphyrins, is nearly planar and the macrocyclic cavity, although reduced compared to porphyrins, allows the complexation of a transition metal such as manganese. Due to its relatively high electron-donating ability, only the manganese(III) complex has been isolated starting from a Mn(II) salt. The geometry and bond distances of complex **2** are also very close to those found in known Mn(III) porphyrins. Considering all these similarities, ligand H_2L_1 could be regarded as a "porphyrin" analog containing pyridine units instead of pyrroles.

In order to check if the structural similarities also gave rise to the same type of chemical properties, we tested the ability of complex **2** to catalyze the epoxidation of alkenes in the presence of an oxidant such as *m*-chloroperbenzoic acid (MCPBA). In a typical reaction, an acetonitrile (CH_3CN, 0.2 ml) solution of MCPBA (99%, 52 μmol) was added to a suspension of complex **2** (2.5 μmol) and cyclohexene (510 μmol) in CH_3CN (0.8 ml) at −40 °C. After 1.5 h at this temperature, the reaction medium was quenched by the addition of triphenylphosphine (104 μmol). The reaction mixture was analyzed by GC and the amount of oxidation products was evaluated with the aid of an internal reference (anisole). The total yield of oxidation products was equal to 78% with respect to the oxidant. Cyclohexene oxide, cyclohexenol and cyclohexenone were present in the relative ratio 20 : 1 : 1. Although some allylic oxidation took place, the selectivity of the epoxidation reaction is good. We also verified that MCPBA alone is unable to epoxidize cyclohexene at this temperature. A subsequent addition of oxidant did not afford more oxidation products, revealing the inactivation of the catalyst. The unstable behavior of complex **2** toward oxidation conditions could be due to the specific reactivity of the cyano groups towards MCPBA, as shown for similar molecules.[6]

In conclusion, we have shown that the Ogawa macrocyclic ligand H_2L_1 is suitable for the complexation of transition metal such as Mn(III). This opens the way to the development of a new generation of ligands in which the cyano groups have been replaced by more inert or bulky substituents in order to prevent self-oxidation of the catalyst. This work is in progress and will be reported in the near future.

Experimental

Preparation of complexes

$[Mn^{III}L_1Cl]$ 1. Ligand H_2L_1 (100 mg, 0.26 mmol), $MnCl_2 \cdot 4H_2O$ (512 mg, 2.6 mmol) and 2,4,6-collidine (171 μl, 1.3 mmol) were heated to 140 °C for 4 h in DMF (20 ml) under nitrogen. Concentration of the DMF solution to 1–2 ml and cooling to 4 °C afforded **1** (95 mg, 70%). Elem. anal. calc. for $C_{24}H_{12}ClN_6Mn \cdot 4H_2O$: C, 52.80; H, 3.43; N, 15.30; Mn, 10.00%. Found: C, 53.02; H, 3.66; N, 15.49; Mn, 10.04%. LSIMS *m*/*z* (%): 439 (100) $[M - Cl]^+$.

$[Mn^{III}L_1(H_2O)_2]OTf$, 2. Complex **1** (100 mg, 0.21 μmol) and Ag^IOTf (0.31 μmol) were stirred at room temperature in anhydrous DMF (7 ml) for 48 h. Filtration on a Celite bed and evaporation of the filtrate to dryness gave a black solid, which was dissolved in warm methanol (1–2 ml) and cooled to 4 °C. The black powder (50 mg) was recovered by filtration, yield 40%. Elem. anal. calc. for $C_{25}H_{16}F_3N_6O_5SMn$: C, 48.08; H, 2.77; N, 13.46; Mn, 8.80%. Found: C, 48.02; H, 2.60; N, 13.10; Mn, 8.46%. LSIMS *m*/*z* (%): 439 (100) $[M - OTf]^+$. UV-Visible (DMF) λ_{max}/nm (ε/$M^{-1}\ cm^{-1}$): 383 (21 665); 483 (6967); 513 (7447); 544sh (5109); 670 (1295).

X-Ray crystal structure determination

Crystal data for **2** ($C_{24}H_{12}N_4Mn \cdot 2H_2O \cdot CF_3SO_3$). Preliminary X-ray precession photographs showed the poor diffracting quality of the crystals. Compound **2** crystallized in the orthorhombic system, space group *Cmcm* or *Cmc*2_1 from the systematic absences. *Cmcm* was assumed and confirmed since refinement in the lowest symmetric space group *Cmc*2_1 does not significantly decrease the reliability factors and standard deviations. $M = 624.432$, $a = 7.986(4)$, $b = 14.969(7)$, $c = 20.429(10)$ Å, $U = 2442(2)$ Å^3, $Z = 4$, μ(Cu-Kα) = 58.8 cm^{-1}, $T = 293$ K, 4996/619 measured/unique reflections ($R_{int} = 0.066$). The triflate anion is disordered across a two-fold axis. It was refined anisotropically with an occupancy of 0.25. The final R_1 was 0.086 for 505 intensities with $I > 2\sigma(I)$, $R_1 = 0.097$ ($wR_2 = 0.251$) for all unique data.

CCDC reference number 151936. See http://www.rsc.org/suppdata/nj/b1/b100169h/ for crystallographic files in CIF or other electronic format.

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