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The Proximal Imidazole Effect on Manganese(III)-Cyclam Complex

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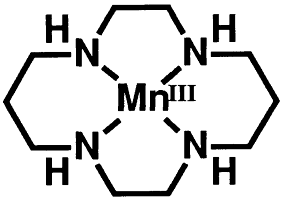
The synthesis, X-ray structure, and chemical properties are reported of a new 5 co-ordinate Mn(III) complex with imidazole-pendant cyclam, which has been found to be an efficient catalyst for alkene epoxidation.

The crucial role of manganese in several biological systems including manganese-requiring redox-active enzymes and Photosystem II[1)] has been stimulating active researches in the biomimetic chemistry of manganese, in particular of porphyrin complexes.[2)]

A saturated macrocyclic N_4 ligand cyclam (= 1,4,8,11-tetraaza-cyclotetradecane) forms a square planar complex **1** with high-spin d^4 Mn(III),[3a)] which, like porphyrin complexes, appears to be useful as catalysts for redox reactions, but few studies have been undertaken. Recently, a bis(μ-oxo) $[(\text{cyclam})\text{MnO}]_2^{3+}$ complex was presented as a potential model for multi-electron redox catalyst.[3b)] It is of interest to see whether **1** can also work as an catalyst for olefin epoxidations, as extensively studied Mn(III)-porphyrin[2)] and Ni(II)-cyclam complexes[4)] in relevance to cytochrome P-450.[5)] We were also interested in whether **1** is activated with proximal donors in these epoxidations, like the porphyrin system.[2)]



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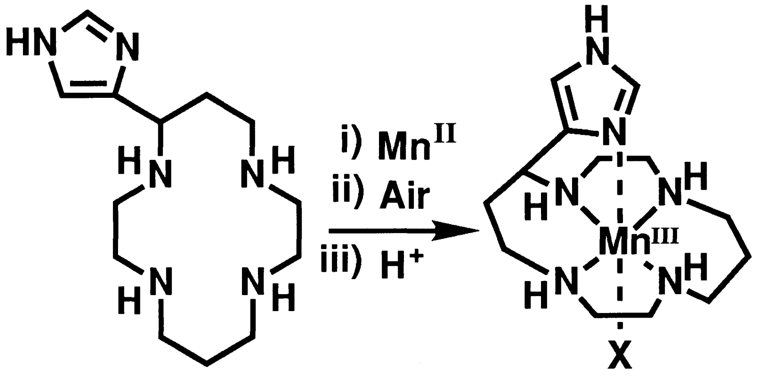

2

3a; X=ClO_4^-
3b; X=Cl^-

A recently explored cyclam with an appended imidazole **2**[6)] may be a suitable ligand to check the proximal imidazole effect. Herein we communicate synthesis, X-ray crystal structure, chemical properties, and catalytic activity in alkene epoxidation of a new Mn(III) complex **3**.

The ligand **2** (0.1 mmol) and equivalent $Mn^{II}(ClO_4)_2 \cdot 8H_2O$ were stirred under air in MeOH at room temperature for 3 h. After addition of a small amount of conc. $HClO_4$ to the resulting light-brown solution, green crystals were obtained. Recrystallization from aqueous $HClO_4$ solution yielded green needles $[Mn^{III}(\mathbf{2})(ClO_4)](ClO_4)_2$ (**3a**), and from aqueous HCl-$HClO_4$ solution green prisms $[Mn^{III}(\mathbf{2})(Cl)](ClO_4)_2$ (**3b**).[7)] The UV-visible spectrum of **3a** showed ligand to Mn^{III} charge transfer absorption at λ_{max} 268 (ε 7860 dm^3 mol^{-1} cm^{-1}) and *d-d* transition at 350 nm (*sh* ε 1600) in pH 3.5 H_2O, which are very similar to those of other d^4 Mn(III) complexes reported in a tetragonally distorted environment (*e.g.* λ_{max} 273 (ε 10500) and 340 nm (*sh* ε 2300) for **1**·$(ClO_4)_3$).[3a,c)] The changes in the molar extinction coefficients (ε) are probably due to the electronic transitions and ε being sensitive to minor steric distortions away from a perfect octahedron. Some evidence of steric distortions due to the intramolecular imidazole co-ordination was observed in the X-ray crystal structure.

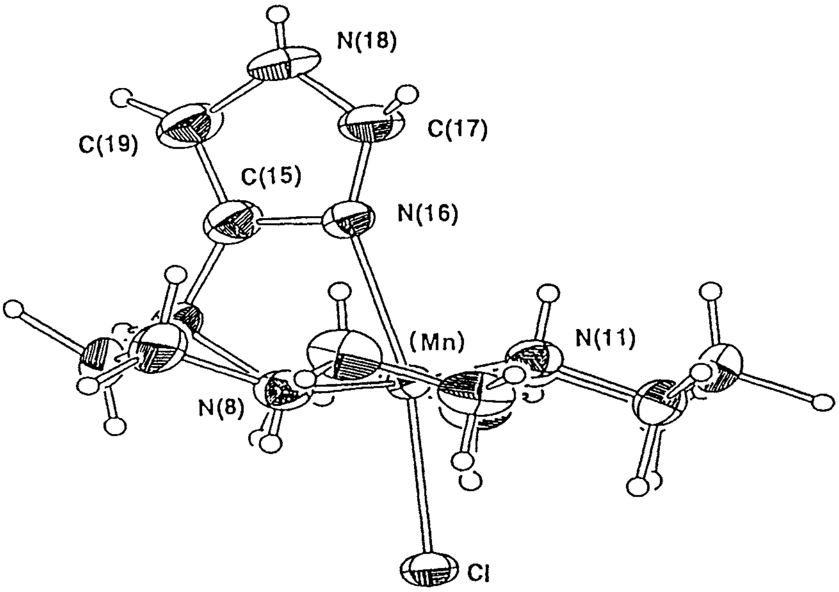

Fig. 1. ORTEP drawing of complex **3b**, side-on view.
Atoms are drawn with 30% probability ellipsoids.

The X-ray crystal structure of **3b** represents the first square planar cyclam complex of Mn(III) with a close imidazole co-ordination from an axial site (Fig. 1).[8)] The Mn(III) atom sits in the cyclam N_4 plane with the imidazole N(16) and chloride ion at axial positions. The imidazole ring stands vertically to the cyclam N_4 plane. The metal-macrocyclic nitrogen bond lengths Mn-N(1), Mn-N(4), Mn-N(8), and Mn-(N11) are 2.039(4), 2.039(4), 2.044(4), and 2.029(4) Å, respectively. In **1** with hexamethyl substituents,[3c)] the mean Mn^{III}-N bond is 2.06 Å. There is a large difference between the axial [Mn-N(16) and Mn-Cl(1) are 2.277(4) and 2.463(2) Å, respectively] and equatorial Mn-N bond distances. This reflects the *Jahn-Teller* distortion for a high-spin d^4 ion.[9)] Earlier, we reported a high spin d^8 nickel(II) complex of **2** (the sixth ligand is CH_3CN) with a closer octahedral structure,[6)] where the equatorial Ni^{II}-cyclam N bond distances (mean 2.07 Å) are a little longer, and the axial Ni^{II}-N(imidazole) (2.098 Å) and Ni^{II}-N(acetonitrile) (2.132 Å) bond distances are much shorter.

The imidazole ligation (in **3a**) does not contribute to stabilization of the Mn^{III} state with respect to Mn^{II}, as found for the porphyrin complexes.[10)] Cyclic voltammetries of **3a** in H_2O (0.1 mol dm^{-3} $NaClO_4$, pH 3.6, 25 °C) showed a quasi-reversible redox wave at $E_{1/2}$ +0.09 V *vs.* saturated calomel electrode (S.C.E.) (ΔE_p 75 mV, scan rate; 500 mV s^{-1}) for $Mn^{III/II}$ couple at a gold electrode. Under the same condition the $Mn^{III/II}$-cyclam has a value of -0.04 V *vs.* S.C.E. **3a** is more easily reduced than **1**, probably due to the π-acceptability of imidazole at an axial position. At slower scan rates below 100 mV s^{-1}, the redox couple became more irreversible to a single reduction wave, indicating the lability of the electrochemically generated Mn^{II} state in the aqueous solution. In both cases, no metal-centered oxidation waves were seen before the solvent limit (*ca.* +1V).

Table 1. Comparison of Catalytic Epoxidation of *trans*-Stilbene with Macrocyclic Mn^{III} and Ni^{II} Complexes

Oxidant	Catalyst[a)]	Turnovers for *trans*-epoxide[b)]
PhIO	**1**	7.6
	3a	9.4
	Cyclam-Ni^{II}	1.6
NaClO	**1**	12
	3a	20
	Cyclam-Ni^{II}	14

[a)] Perchlorate salts were used for both Mn(III)- and Ni(II)-cyclam complexes.

[b)] Mole of product / mole of catalyst in 1 h. Other minor products (PhCHO and unidentified products) were also detected.

In a typical experiment of the oxidation catalysis using NaClO, 0.16 mmol *trans*-stilbene, 4 µmol catalyst, and 6 µmol benzyl tri-n-butylammonium chloride (phase-transfer-catalyst) in 0.4 ml of CH_2Cl_2 were stirred vigorously with 0.8 ml of 0.74 mol dm^{-3} NaClO (domestic bleach, pH 12.7) at 25 °C for 1 h. For the PhIO reaction, 0.4 mmol *trans*-stilbene, 1.0 mmol PhIO, 2 µmol catalyst were stirred in 2 ml of anhydrous CH_3CN under Ar at 25 °C for 1 h. As a result, a novel catalyst **3a** more efficiently catalyzes the oxygen atom transfer from both PhIO and NaClO to the substrate than unsubstituted Mn(III)-cyclam **1** and Ni(II)-cyclam complexes,$^{4a-c)}$ as shown in Table 1. The proximal imidazole increases the catalytic turnover, as found for porphyrins.$^{11)}$ Although we tentatively postulate an oxenoid intermediate, (*trans*-cyclam)Mn^{V}=O species, like the (porphyrin)$Mn^{IV\text{ or }V}$=$O^{12)}$ and (cyclam)Ni^{IV}=O,$^{4a,c)}$ detailed mechanistic studies are currently in progress.

Further work of the rigid and well-defined Mn(III) donor pendant-cyclam complexes will increase knowledge of the Mn co-ordination chemistry and lead to better understanding of the catalytic activities of Mn(III)-porphyrin complexes.

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7) Elementary analyses (C, H, N) of these metal complexes were satisfactory.
8) *Crystal Data* for **3** (X = Cl): space group $P\bar{1}$; a = 10.220(1), b = 11.999(1), c = 9.615(1) Å, α = 101.24(1), β = 96.17(1), γ = 97.42(1)°; U = 1136 $Å^3$; Z = 2; D_c = 1.624 g cm^{-1}; $\mu(CuK_\alpha)$ = 87.0 cm^{-1}; No. of intensities mesured, 3869; no.of data, 3437 ($|F_o| > 4\sigma(F_o)$); $R(R_W)$ = 0.066 (0.099).
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