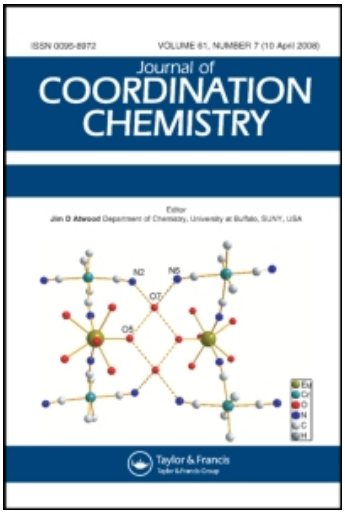

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Manganese complexes with a lengthy o -xylylene cross-bridged cyclam ligand: synthesis, characterization and catalytic hydrogen abstraction by dioxygen activation

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Manganese complexes with a lengthy *o*-xylylene cross-bridged cyclam ligand: synthesis, characterization and catalytic hydrogen abstraction by dioxygen activation

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Two ultra rigid, *o*-xylylene cross-bridged macrobicyclic ligands, 1,10,13,19-tetraazatricyclo [8.6.6.$0^{3,8}$]docosa-3,5,7-triene (H_2XBC), and 13,19-dimethyl-1,10,13,19-tetraazatricyclo [8.6.6.$0^{3,8}$]docosa-3,5,7-triene (Me_2XBC), have been synthesized and the manganese complexes have been synthesized and characterized, including an X-ray structure determination. Mn(Me_2XBC)Cl_2 displays a relatively high redox potential for the Mn^{2+}/Mn^{3+} couple (+0.947 V vs SHE, measured in CH_3CN), suggesting that the manganese(III) complex may be capable of hydrogen abstraction from moderately active substrates. Direct reaction of the freshly synthesized manganese(III) complex, [Mn(Me_2XBC)Cl_2]PF_6, with 1,4-cyclohexadiene confirmed its hydrogen abstracting ability. The manganese(II)/Me_2XBC complex is activated by dioxygen in buffered basic aqueous solutions and catalyzes hydrogen abstraction from selected substrates. A possible mechanism for this manganese complex catalyzed dioxygen activation and hydrogen abstraction is proposed.

Keywords: Manganese complex; Bridged cyclam; Hydrogen abstraction; Catalytic oxidation

1. Introduction

Exploitation of metal complexes with enabling ligands and their applications in catalysis is important for both the understanding and applications of chemistry [1]. Both thermodynamic and kinetic stabilities of metal complexes are important in determining their utility in catalysis [2]. Generally, the stabilities of metal complexes increase with increasing topological constraints built into the ligand, in the sequence: monodentate ligands <linear or branched chelating ligands < macrocyclic ligands <macrobicylic ligands or cryptates [2a]. This reflects the well known structural relationship: chelating effect <macrocyclic effect <cryptate effect. Metal cryptate complexes have no free sites for reacting with oxidant or substrate making them less useful in catalysis. Consequently, macrocylic ligands and linear or branched chelating

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ligands are best for catalysis. Examples of such oxidation catalysts include porphyrin ligands [3, 4], which serve as the active sites of many oxidation enzymes, in addition to other natural functions, and have been extensively mimicked and applied in catalytic oxidations using synthetic ligands. Bis(salicylal-ethylenediimine), Salen, the prototype of tetra- and pentadentate Schiff-base ligands, have also been successfully applied in asymmetric oxidations [5, 6].

In addition to the cryptands that totally enclose metal ions, a second kind of macrobicyclic ligand binds metal ions very strongly, but leaves two *cis* sites empty and available for interaction with substrate or oxidant. These *bridged macrocycles* have been applied extensively in catalysis [7]. Weisman and collaborators pioneered in the synthesis of the cross-bridged cyclams, first reporting their copper and zinc complexes and investigating their application in radiopharmaceuticals [8, 9]. Transition metal complexes with the ethylene cross-bridged cyclam ligand, Me_2EBC (4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane), were studied in these laboratories [10, 11], because their kinetic stabilities were expected to be exceptionaly high. That expectation was fulfilled even with such labile metal ions as manganese(II) [10d, f]. Furthermore, the manganese complex, $Mn(Me_2EBC)Cl_2$, revealed an unexpected oxygen transfer mechanism in which the hydrogen peroxide adduct of the manganese(IV) complex transfers oxygen directly to olefinic substrates by a Lewis acid pathway that was previously proven only for early transition metal ions whose oxidation states are not so easily changed, such as Ti(IV), V(V), Mo(VI) and W(VI). Further, the manganese(IV) complex, $[Mn^{IV}(Me_2EBC)(OH)_2]^{2+}$, displays a gentle oxidizing ability, and can abstract hydrogen atoms only from C–H bonds with bond dissociation energies below $82\,kcal\,mol^{-1}$. In addition, these well-characterized Mn(II), Mn(III) and Mn(IV) complexes have structural features of value to the understanding of natural systems, for example, water oxidation in photosystem II. Since the structure of the tetramanganese core of the OEC consists of a trinuclear cluster attached by a single μ-oxo bridge to the fourth appended manganese atom, attention has focused on the monomeric manganese appendage as the site of the water oxidation event [12e]. The previously reported Mn(IV) complex of Me_2EBC is a rare example of a relatively simple molecular entity containing the Mn^{IV}-OH and Mn^{IV}=O, functional groups that may be related to those of the monomeric appendage, and its important chemistry. To further explore metal complexes with cross-bridged macrocyclic ligands, the studies presented here feature ligands having a more lengthy cross-bridged linker, o-xylylene, and the application of their manganese complexes in biomimetic oxidations using dioxygen as the terminal oxidant.

2. Experimental section

All reagents were purchased from Aldrich. $MnPy_2Cl_2$ [13], and 1,4,8,11-tetraazacyclotetradecane-5,12-dione were prepared according to the literature [14]. All solvents were of reagent grade and dried and purified, when necessary, by accepted procedures [15]. Elemental analyses were performed by Quantitative Technologies, Inc. Mass spectra (fast atom bombardment) were measured by the Analytical Service Group of the University of Kansas on a VG ZAB HS spectrometer equipped with a xenon gun. Several matrices are available, including NBA (nitrobenzyl alcohol),

TG/G (thioglycerol-glycerol), and GLY (glycerol). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX400 spectrometer. All spectra were referenced internally to tetramethylsilane (δ 0.00 ppm) or to the residual solvent resonances.

Electrochemical experiments were run on an electrochemical analyzer from CH Instruments in dry acetonitrile at room temperature under nitrogen. Tetrabutylammonium tetrafluoroborate (0.1 M) was used as the supporting electrolyte. A Pt button was used as the working electrode with a Pt-wire as the counter electrode, and a non-aqueous Ag-wire pseudo-reference electrode.

2.1. *Synthesis of 1,10,13,19-tetraazatricyclo[8.6.6.0^{3,8}]docosa-3,5,7-triene-14, 20-dione (2)*

The synthetic procedure for this compound was modified from a literature method [14]. In a two-neck flask (2 L) were charged 1,4,8,11-tetraazacyclotetradecane-5,12-dione (**1**) (10 mmol), Na_2CO_3 (100 mmol) and dry CH_3CN (1 L). The mixture was heated to reflux under N_2 and α,α'-dibromo-*o*-xylene (10 mmol) in CH_3CN (50ml) was added via a syringe pump over a two day period. The reaction mixture was filtered warm and the filtrate was evaporated to dryness on a rotary evaporator. The crude product was purified by chromatography on silica gel (CH_2Cl_2/CH_3OH, 95:5). The appropriate fractions were collected and evaporated to dryness under reduced pressure to yield the expected product, **2** (yield 35%), as a white solid. Anal. Calcd for $C_{18}H_{26}N_4O_2$ (%): C, 65.43; H, 7.93; N, 16.96. Found: C, 64.80; H, 8.06; N, 16.72. ^{1}H NMR ($CDCl_3$): 1.98 (s, 2H), 2.40–2.49 (m, 4H), 2.65–2.75 (m, 6H), 2.93–2.96 (m, 2H), 3.13–3.17 (m, 2H), 3.56–3.59 (m, 2H), 3.68 (s, 4H), 7.20–7.23 (m, 2H), 7.32–7.34 (m, 2H), 8.87 (s, 2H). ^{13}C NMR ($CDCl_3$): 33.37, 36.80, 50.43, 51.04, 57.19, 128.74, 135.72, 136.80, 172.27. FAB$^+$ mass spectrum (CH_2Cl_2): 331 $[L02H]^+$.

2.2. *Synthesis of 1,10,13,19-tetraazatricyclo[8.6.6.0^{3,8}]docosa-3,5,7-triene (3, H_2XBC)*

Compound **2** (20 mmol) was placed in a two-neck flask (300 mL). BH_3 in THF (1 M, 200 mL) was added via a syringe under N_2 and the stirred mixture was kept in an ice bath for 0.5 h, and then heated to reflux overnight. The excess BH_3 in THF was removed by distillation and the remaining oil was treated with 3M HCl (40 mL) in an ice bath. The mixture was refluxed for 3 h and the hydrochloric acid solution was evaporated to dryness in a rotary evaporator. The residue was treated with 10 M NaOH (50 mL), extracted with $CHCl_3$ (3 × 100 mL) and the combined organic phase was dried over Na_2SO_4. After filtration, the filtrate was evaporated to dryness in a rotary evaporator and the crude product was purified by chromatography on neutral alumina gel (CH_2Cl_2/CH_3OH, 95:5). The appropriate fractions were collected and evaporated to dryness under reduced pressure to yield a white to yellow sticky solid. The anhydrous free base form of the ligand (compound **3** H_2XBC) may be obtained by distillation over KOH pellets under vacuum and stored in the glove box. Yields 40–50%. Anal. Calcd for $C_{18}H_{30}N_4$ (%): C, 71.48; H, 10.00; N, 18.52. Found: C, 71.54; H, 10.14; N, 18.59. ^{1}H NMR ($CDCl_3$): 1.51–1.60 (m, 2H), 1.66–1.74 (m, 2H), 2.23–2.28 (m, 2H), 2.37–2.43 (m, 2H), 2.53–2.87 (m, 14H), 3.59–3.66 (m, 4H),

7.24–7.26 (m, 4H). ^{13}C NMR ($CDCl_3$): 25.35, 47.86, 51.58, 55.24, 57.83, 59.27, 127.81, 134.83, 138.58. FAB^+ mass spectrum ($CHCl_3$): 303 $[L2H]^+$.

2.3. *Synthesis of 13,19-dimethyl-1,10,13,19-tetraazatricyclo[8.6.6.0^{3,8}] docosa-3,5,7-triene (4, Me_2XBC)*

Compound **3** (10 mmol) was dissolved in a formic acid (30 mL)/formaldehyde (20 mL) solvent. The mixture was refluxed overnight and the subsequent work-up was similar to the preceding procedure. Compound **4** (Me_2XBC) was obtained as a yellow and very hygroscopic solid. Crystals of the free ligand H_2XBC suitable for X-ray diffraction were obtained by the diffusion of diethyl ether into a saturated acetonitrile solution of H_2XBC in the glove box. Anhydrous **4** may be obtained by distillation over KOH pellets in vacuo and stored in the glove box. Yields 65–75%. Anal. Calcd for $C_{20}H_{34}N_4$ (%): C, 72.68; H, 10.37; N, 16.95. Found: C,72.53; H, 9.66; N, 16.90. ^{1}H NMR ($CDCl_3$): 1.44–1.45 (m, 4H), 2.13–2.20 (m, 10H), 2.30–2.54 (m, 12H), 3.80 (br s, 4H), 7.15–7.26 (m, 4H). ^{13}C NMR ($CDCl_3$): 23.64, 43.95, 52.58, 53.11, 53.18, 55.61, 59.32, 127.25, 133.87, 139.80. FAB^+ mass spectrum (CH_3CN): 331 $[L22H]^+$.

2.4. *Synthesis of $[Mn(H_2XBC)_2(\mu\text{-}Cl)]_2Cl_2$*

$MnPy_2Cl_2$ (0.42 g) was added to the stirred solution of **3** (0.42 g) in dry CH_3CN (30 mL) in the glove box. The metal salt dissolved quickly (~5 min) to yield a pale yellow solution. After stirring overnight, a large amount of off-white solid precipitated, was collected by filtration, washed with ~3 mL of CH_3CN and dried in vacuo. Yield 0.32 g, 63%. Anal. Calcd for $[Mn(H_2XBC)Cl_2]$ (%): C, 50.57; H, 7.08; N, 13.11; Cl 16.55. Found: C, 50.79; H, 7.29; N, 12.98; Cl, 16.64. FAB^+ mass spectrum (CH_3OH): 355 $[Mn(H_2XBC)]^+$, 392 $[Mn(H_2XBC)Cl]^+$.

2.5. *Synthesis of $Mn(Me_2XBC)Cl_2$*

$MnPy_2Cl_2$ (0.57 g) was added to the stirred solution of **4** (0.69 g) in warm CH_3CN (15 mL) in the glove box. The metal salt dissolved and a large amount of white precipitate formed immediately. After stirring over night, the white precipitate was filtered, washed with ether and dried in vacuo. Yield 0.75 g, 82%. Anal. Calcd for $[Mn(Me_2XBC)Cl_2]$ (%): C, 52.64; H, 7.51; N, 12.28; Found: C, 52.46; H, 7.29; N, 12.26. FAB^+ mass spectrum (CH_3OH): 420 $[Mn(Me_2XBC)Cl]^+$. Crystals suitable for X-ray diffraction were obtained by dissolving the complex in CH_3OH, followed by standing in the glove box for a few days.

2.6. *Synthesis of $[Mn(Me_2XBC)Cl_2]PF_6$*

$NOPF_6$ (0.20 g) was added to the stirred solution of $Mn(Me_2XBC)Cl_2$ (0.456 g) in CH_3CN (8 mL) in the glove box. Gas evolved and the colorless solution turned deep yellow. After stirring for 1 h, ether (50 mL) was added to yield a deep red oil. The supernate was decanted and the residual oil was dried in vacuo to yield a yellow–brown solid. The solid was recrystallized by the diffusion of diethyl ether into

a saturated acetonitrile solution of $[Mn(Me_2XBC)Cl_2]PF_6$. Yield 0.58 g, 96%. Anal. Calcd $[Mn(Me_2XBC)Cl_2]PF_6 \cdot CH_3CN$ (%): C, 41.13; H, 5.81; N, 10.9; Cl, 11.04. Found: C, 41.07; H, 5.79; N, 10.51; Cl, 10.51. FAB^+ mass spectrum (CH_3CN): 456 $[Mn(Me_2XBC)Cl_2]^+$

2.7. *Crystal structure analysis*

All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Cu–Kα (Au: Cu) radiation and a rotating anode generator. The data were corrected empirically for variable absorption effects using psi scans for three reflections; the relative transmission factors ranged from 0.947 to 1.000. The Brüker software package SHELXTL was used to solve the structure using ''direct methods'' techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2data with the SHELXTL Version 6.10 software package. The X-ray structure of H_2XBC is shown in figure 1, the crystal data and structure refinement are listed in table 1, the intramolecular hydrogen bond lengths and angles are listed in table 2, and the whole crystal information is attached in Supporting Information. The X-ray structure of $Mn(Me_2XBC)Cl_2$ is shown in figure 2 and the packing diagram for this complex is shown in figure 3. The crystal data and structure refinement are listed in table 1, the selected bond lengths and angles are listed in table 3, and the whole crystal information is attached in supporting information.

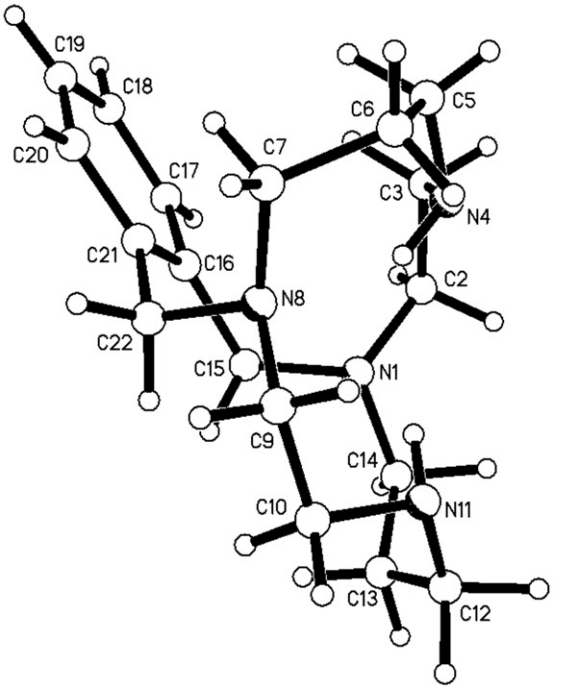


Figure 1. The X-ray structure of H_2XBC.

Table 1. Crystal data and structural refinements for H_2XBC and $Mn(Me_2XBC)Cl_2$.

Empirical Formula	$C_{18}H_{30}N_4$ (H_2XBC)	$MnCl_2C_{20}H_{34}N_4 \cdot (CH_3OH)_{0.5}$
Formula Weight	302.46	472.37
Crystal Dimensions (mm)	$0.40 \times 0.30 \times 1.00$	$0.30 \times 0.15 \times 0.50$
Crystal System	monoclinic	Triclinic
Space Group	$P2_1/n$	P–1
Completeness to theta = 60.09(deg)	100.0%	100.0%
a/Å	11.459(3)	9.049(2)
b/Å	16.759(4)	12.913(2)
c/Å	9.681(3)	19.434(2)
β (deg)	112.28(1)	86.589(14)
Vol/Å^3, Z	1720.3(8), 4	2237.0(7), 4
D(calcd) g cm^{-3}	1.168	1.403
F_{000}	664.00	1000.00
Absorption coefficient (mm^{-1})	0.542	7.115
Temperature (K)	296	151
Refln total	2692	5944
Independent reflections	2552	5635
Refinement method	Full-matrix on F^2	Full-matrix on F^2
Data/restraints/parameters	2552/0/324	5635/0/514
R indices (all data): *R*; Rw	0.063; 0.136	0.127; 0.161
Goodness of fit (F^2)	1.084	0.963
Largest diff. peak and hole/eÅ^{-3}	0.188, −0.175	0.81, -0.52

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$
$wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table 2. Hydrogen bonds for H_2XBC [Å and deg].

D–H . . . A	d(D–H)	d(H . . . A)	d(D . . . A)	<(DHA)
N(4)–H(4) . . . N(8)	0.87(3)	2.22(3)	2.968(3)	143(2)
N(4)–H(4) . . . N(1)	0.87(3)	2.35(3)	2.811(3)	112.8(19)
N(11)–H(11) . . . N(1)	0.92(3)	2.36(3)	3.142(3)	143(2)

2.8. *General procedure for catalytic oxidation*

A glass U-shaped tube-reactor equipped with a *dry ice* cooled condenser was charged with a CHES (2-(cyclohexylamino)ethanesulfonic acid) buffered solvent mixture (5 mL) of acetone/water (ratio 4:1, pH ~10.5) and the catalyst (2 mM) and substrate (56 mM). Air was bubbled through the reaction mixture for 16 h with the temperature controlled (water bath) at 35°C. Product analysis was performed using GC by the internal standard method and products were identified by GC–MS. A parallel experiment without catalyst was carried out as a control.

3. Results and discussion

3.1. *Ligand strategies*

Previous to this work, studies of transition metal complexes having ethylene as the 2-carbon bridging group in the cross-bridged cyclam ligand were reported from these laboratories. Some of those complexes showed unexpected catalytic properties in hydrogen abstraction and oxygen transfer processes [10–12], motivating further

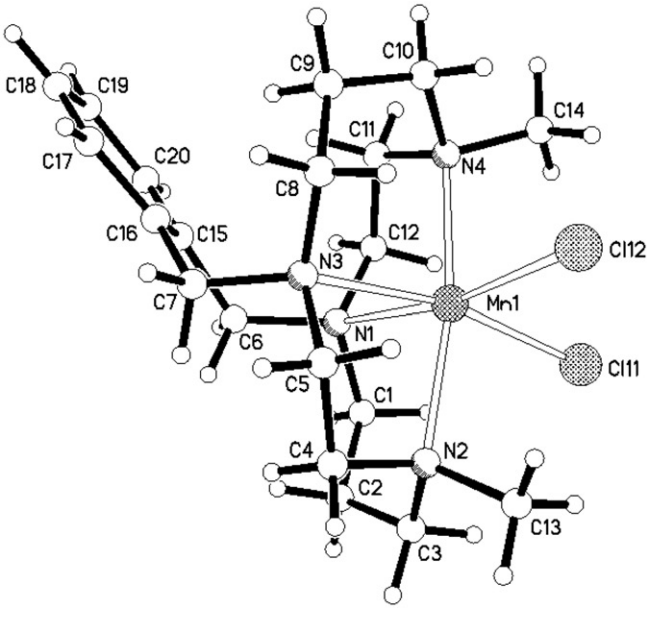


Figure 2. The X-ray structure of $Mn(Me_2XBC)Cl_2$.

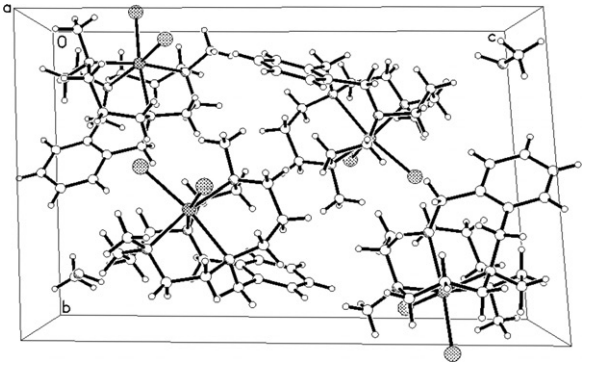
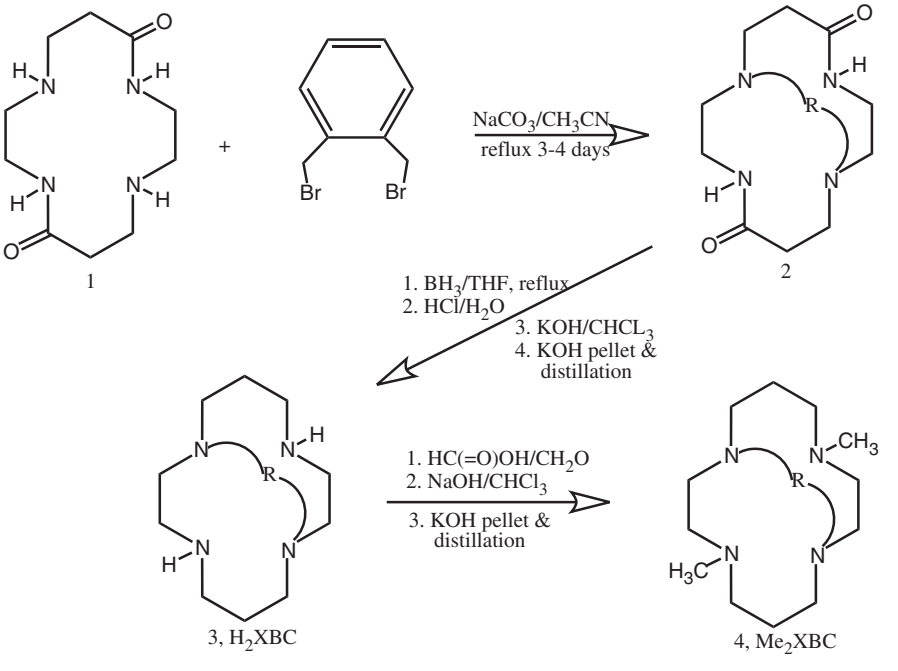


Figure 3. The packing diagram of $Mn(Me_2XBC)Cl_2$.

Table 3. Selected bond lengths (Å) and angles (deg) for $Mn(Me_2XBC)Cl_2$.

Mn(1)–N(4)	2.230(5)	N(3)–Mn(1)–N(1)	84.99(18)
Mn(1)–N(2)	2.258(5)	N(4)–Mn(1)–Cl(12)	89.75(14)
Mn(1)–N(3)	2.406(5)	N(2)–Mn(1)–Cl(12)	97.62(15)
Mn(1)–N(1)	2.433(5)	N(3)–Mn(1)–Cl(12)	93.27(14)
Mn(1)–Cl(12)	2.510(2)	N(1)–Mn(1)–Cl(12)	169.93(14)
Mn(1)–Cl(11)	2.523(2)	N(4)–Mn(1)–Cl(11)	97.87(14)
N(4)–Mn(1)–N(2)	170.30(19)	N(2)–Mn(1)–Cl(11)	88.25(14)
N(4)–Mn(1)–N(3)	92.54(19)	N(3)–Mn(1)–Cl(11)	168.50(14)
N(2)–Mn(1)–N(3)	80.80(19)	N(1)–Mn(1)–Cl(11)	91.89(13)
N(4)–Mn(1)–N(1)	80.44(19)	Cl(12)–Mn(1)–Cl(11)	91.68(7)
N(2)–Mn(1)–N(1)	91.90(19)		

explorations in which other bridging groups were used in similar macrobicyclic ligands. The catalytic properties of the complex of such a new ligand are reported here. According to Guilard [16]. the electrophilic *m*-xylylene moiety can be linked intramolecularly across the cyclam ring by binding to *trans*-located amine nitrogen atoms of a *trans*-dioxocyclam to form the *trans*-dioxomacrobicyclic ligand, which could then be reduced by borane in THF to the desired macrobicyclic ligand. Under similar reaction conditions, we successfully added an *o*-xylylene bridge to a *trans*-dioxocyclam producing the *trans*-dioxomacrobicyclic ligand, 1,10,13,19-tetraazatricyclo[8.6.6.$0^{3,8}$]docosa-3,5,7-triene-14,20-dione (**2**) (scheme 1) [17]. Reduction of **2** produced the expected macrobicyclic ligand, 1,10,13,19-tetraazatricyclo[8.6.6.$0^{3,8}$]docosa-3,5,7-triene (**3**, H_2XBC). Methylatio [18] of H_2XBC proceeded smoothly at the two secondary nitrogen atoms and produced the desired ligand, 13,19-dimethyl-1,10,13,19-tetraazatricyclo[8.6.6.$0^{3,8}$]docosa-3,5,7-triene (**4**, Me_2XBC), in high yields. This synthetic system is summarized in and described in detail in the experimental section. The anhydrous free ligand H_2XBC, obtained in this way, is a white solid, while Me_2XBC is a sticky yellow oil at room temperature. Crystals of the free ligand H_2XBC suitable for X-ray diffraction were obtained by diffusion of diethyl ether into a saturated solution of H_2XBC in hot acetonitrile in the glove box. The crystal structure clearly shows that the pure ligand adopts a U-shaped conformation with the non-bridged N atoms (N4 and N11) oriented towards the cleft. This structure is similar to that of the precursor, 1,10,13,19-tetraazatricyclo[8.6.6.$0^{3,8}$]docosa-3,5,7-triene-14,20-dione (**2**). To our knowledge, this is the first example of a crystal structure of an anhydrous free ligand of this class. All the related ligand crystal structures are those of the protonated and/or hydrated ligands. [7c,e,f,h,i;8a,10c,d,19] This ligand structure provides better insight into the accommodation of the metal ion by the ligand upon complexation.



Scheme 1. Ligand synthesis.

3.2. *Manganese complexes*

The challenge associated with forming manganese and iron complexes with the new ligand were reminiscent of those encountered with the first ligand of this class, ethylene cross-bridged cyclam [10f]. It was soon found that neither hydrated nor protonated H_2XBC, would form a metal complex with the manganese cation. As in the earlier case, the new ligands are properly described as "proton sponges". The same techniques that were found to be necessary for Me_2EBC had to be applied to the synthesis of the manganese complexes of H_2XBC and Me_2XBC. Accordingly, by employing dry aprotic solvents, an inert atmosphere, and an anhydrous divalent manganese salt, $Mn(py)_2Cl_2$, the pure manganese complexes of H_2XBC and Me_2XBC were synthesized in high yields. The manganese(III) complex of Me_2XBC was conveniently synthesized by oxidation of $Mn(Me_2XBC)Cl_2$ with $NOPF_6$. The crystal structure of $Mn(Me_2XBC)Cl_2$ was solved and selected bond lengths and angles are summarized in table 2. The X-ray structure for $Mn(H_2XBC)Cl_2$ was also solved but the data were too poor to permit the calculation of bond lengths and angles. Attempts to grow single crystals of the manganese(III) complex have been unsuccessful.

The coordination chemistries of the tetradentate ligands H_2XBC and Me_2XBC with the manganese(II) cation are strikingly different, but the complexes of Me_2XBC and Me_2EBC are very similar. Although the manganese cations are pseudo-octahedral in both complexes, the H_2XBC derivative is a dimer, with its two manganese atoms bridged by a pair of chlorides. Like $Mn(Me_2EBC)Cl_2$, the $MnCl_2$ complex of Me_2XBC is a monomer because the two methyl substituents inhibit the formation of dimeric structures. This structural difference between the manganese complexes of H_2XBC and Me_2XBC was confirmed by the composition of the products of reactions with NH_4PF_6 in MeOH. Both chlorides of $Mn(Me_2XBC)Cl_2$ were replaced by PF_6 anions, but only one of the two chlorides was replaced in the H_2XBC complex (equation 1).

$$[Mn(H_2XBC)(\mu - Cl)]_2(Cl)_2 + 2NH_4PF_6 \rightarrow [Mn(H_2XBC)(\mu - Cl)_2](PF_6)_2 + 2NH_4Cl \quad (1)$$

The structure of $Mn(Me_2XBC)Cl_2$ is similar to that of the corresponding ethylene cross-bridged manganese(II) complex, $Mn(Me_2EBC)Cl_2$ [10f]. In both structures, the manganese cations adopt distorted octahedral geometries with the macrobicycle occupying two axial and two *cis* equatorial sites while the two chlorides occupy the other two *cis* equatorial sites. The Mn^{2+} is more deeply embedded within the cavity of the larger Me_2XBC than in the ethylene cross-bridged complex. The N_{ax}–Mn–N_{ax}, N_{eq}–Mn–N_{eq} bond angles in $Mn(Me_2XBC)Cl_2$ are 170.2(3)° and 85.0(2)°, respectively, while they are 158.0(2)° and 75.6(2)° in $Mn(Me_2EBC)Cl_2$. The pairs of similar Mn–N bond lengths in $Mn(Me_2EBC)Cl_2$ are more nearly identical, i.e., 2.325(4) Å, 2.332 Å, 2.333 Å and 2.347 Å, while they are obviously different in the $Mn(Me_2XBC)Cl_2$ complex. The lengths of N_{eq}-Mn bonds are longer than those of N_{ax}–Mn bonds, that is, 2.397(6) Å and 2.438(7) Å *versus* 2.246(7) Å and 2.226(7) Å. These differences must be traceable to the fact that the *o*-xylylene cross linker is a four atom group and, despite its confined shape, still longer than the 2-carbon ethylene linker. These differences in the coordination sphere of the metal ion should affect such properties as redox potentials.

Indeed, electrochemical studies of the new complex in acetonitrile showed that the Mn^{3+}/Mn^{2+} couple for $Mn(Me_2XBC)Cl_2$ occurs at a much higher redox potential (+0.947 V *vs* SHE with peak separation of 78 mV) than that of $Mn(Me_2EBC)_2Cl_2$

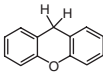
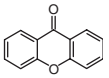
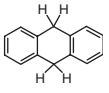
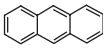
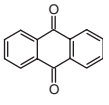
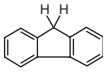
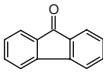
(+0.585 V) [10f, j]. Also, no obvious Mn^{4+}/Mn^{3+} couple was detected for $Mn(Me_2XBC)Cl_2$ (figure 4). The high redox potential of this Mn^{3+}/Mn^{2+} couple suggests that the manganese(III) complex of Me_2XBC may serve as a reactive intermediate for oxidation reactions (vide infra).

3.3. *Catalytic oxidation*

Because of the unusual (for manganese) catalytic oxidation chemistry of $Mn(Me_2EBC)_2Cl_2$, as briefly described in the introduction, the first experiments with the new xylylene bridged derivative, $Mn(Me_2XBC)Cl_2$, were designed to study the oxidation process that has been well characterized for the ethylene bridged homolog; i.e., catalytic hydrogen abstraction using H_2O_2 as the oxidant in acetone/water solution, at any pH between ~2 and ~10. Under these conditions, hydrogen abstraction from 1,4-cyclohexadiene did occur and the two manganese catalysts demonstrated very similar reactivities. For example, in buffered acetone/water (1 : 1, pH ~10), with $Mn(Me_2XBC)Cl_2$ as the catalyst, 1,4-cyclohexadiene was 56.7% converted with a 23.6% yield of benzene as the hydrogen abstraction product, while the $Mn(Me_2EBC)_2Cl_2$ catalyst provided 52.9% conversion with a 24.5% yield of benzene. Oxygenation products were also found, including the mono-epoxide and di-epoxide of 1,4-cyclohexadiene. However, unlike $Mn(Me_2EBC)Cl_2$, upon addition of H_2O_2 the solution containing $Mn(Me_2XBC)Cl_2$ did not change into the violet color characteristic of the Mn^{IV} complex of Me_2EBC. In view of the relatively high potential for the Mn^{3+}/Mn^{2+} couple of the new complex, it was reasonable that H_2O_2 failed to oxidize the manganese ion to an oxidation state higher than Mn(III). Understanding began when it was shown that the pure manganese(III) complex, $[Mn(Me_2XBC)Cl_2]PF_6$, reacts with 1,4-cyclohexadiene at high pH (buffered acetone/water (ratio 4 : 1, pH~10.5), giving a 26% yield of benzene based on the manganese(III) complex. It was also soon found that dioxygen can be used as the terminal oxidant with this catalyst, and that the catalyst system only operates in basic media.

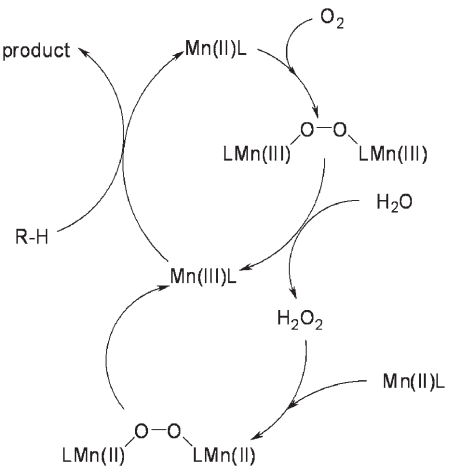
After a small increase in the reaction temperature, adjustment to basic pH, and switching to the oxygen in air as oxidant, the new catalyst system was found to oxidize a number of selected substrates giving products associated with removal of hydrogen atoms from the substrates. No catalytic substrate oxidation occurs in neutral or acidic solution or in the absence of catalyst. In fact, the manganese(II) complex, $Mn(Me_2XBC)Cl_2$, is not oxidized by dioxygen in neutral or acidic solution. Efficient catalytic hydrogen abstraction using O_2 as the oxidant was observed in buffered basic solutions (~35°C, acetone/water (4 : 1) with CHES (2-cyclohexylamino)ethanesulfonic acid, pH~10.5; O_2 bubbled through solution for 16 h), and the results are summarized in table 4. Catalytic hydrogen abstraction from 1,4-cyclohexadiene (BDE_{CH} 76 kcal mol^{-1}) provided a 32.2% yield of benzene as the sole product, while xanthene (BDE_{CH} 75.5 kcal mol^{-1}) provided 62.5% of xanthone. With 9,10-dihydroanthracene (BDE_{CH} 78 kcal mol^{-1}) as the substrate, 58.5% of anthraquinone and 3.9% of anthracene were obtained due to O_2 capture and further hydrogen abstraction from intermediates. No 9,10-dihydroxyanthracene was detected. Fluorene (BDE_{CH} 80 kcal mol^{-1}) produced only 14% of 9-fluorenone as the sole product. No product and no consumption of substrate were observed with diphenyl methane (BDE_{CH} 82 kcal mol^{-1}) as the substrate.

Table 4. Catalytic Hydrogen abstraction with $Mn(Me_2XBC)Cl_2$ Using Dioxygen.

Run	Substrate	BDE_{CH} ($Kcal\,mol^{-1}$)	Product	Yield (%)
1		75.5		62.5
2		76		32.2
3		78		3.9
				58.5
4		80		14
5	Diphenyl methane	82	–	–

Reaction conditions: 5 mL buffered solvent mixture (acetone/water ratio 4 : 1, pH ~10.5), substrate 56 mM, catalyst 2 mM, 35°C, air was bubbled through the solution for 16 h.

Discussion thus far has focused on the differences between two siblings in the family of bridged cyclams, but there is also a provocative similarity in their behaviors. The catalytic hydrogen abstracting abilities demonstrated here for the Mn^{3+}/Mn^{2+} couple of the new Me_2XBC catalyst are very similar to those of the activated form of the Me_2EBC catalyst, $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$, which involves the corresponding Mn^{4+}/Mn^{3+} couple, as reported elsewhere [12d]. Remarkably, both catalyst systems can oxidize any of the same set of substrates having C–H bond dissociation energies less than $82\,kcal\,mol^{-1}$, and both fail to oxidize substrates having $BDE_{CH} > 82\,kcal\,mol^{-1}$ over periods of many days. At the present time this similarity can only be treated as coincidental. Meaningful comparison between the activated Me_2EBC and Me_2XBC complexes is hindered by the fact that we have been unsuccessful in attempts to isolate and characterize the dihydroxy complex, $Mn^{III}(Me_2XBC)(OH)_2{}^+$, or any of it's acid-base complements. Only the dichloro complex of manganese(III), $Mn^{III}(Me_2XBC)Cl_2{}^+$, is available for detailed study. Further, it is not clear which, if any, of the equilibrium related species is dominant under the reaction conditions for the catalytic measurements: $Mn^{III}(Me_2XBC)Cl_2{}^+$, $Mn^{III}(Me_2XBC)Cl(OH)^+$ $Mn^{III}(Me_2XBC)(OH)_2{}^+$, or, again, any of their acid-base complements. In the context of the Polyani principle [20], the corrected standard potential of 0.947V and the observed behavior (sharp decline in hydrogen abstraction at $82\,kcal\,mol^{-1}$), suggest the possibility that the dichloro



Scheme 2. Proposed mechanism for oxygen activation and hydrogen abstraction catalyzed by $Mn(Me_2EBC)Cl_2$.

complex of Mn^{III} is the reactive species in the oxidations reported in table 4. Qualitatively, the combined results predict that the bond between the abstracted hydrogen atom and the ligated atom of the catalyst should be much more acidic than is usually the case for water bound to divalent transition metal ions.

Rate measurements for systems containing a substrate, O_2 and the $Mn(Me_2XBC)Cl_2$ catalyst revealed no obvious induction period prior to hydrogen abstraction from 1,4-cyclohexadiene. On that basis and the information presented above, a possible mechanism for catalytic O_2 oxidation by $Mn(Me_2XBC)Cl_2$ is suggested in scheme 2. A pair of one-electron processes between O_2 and two molecules of manganese(II) complex first produces the peroxide-bridged bis{manganese(III)} dimer, a process that is well known from the reactions of cobalt(II) and iron(II) with O_2 [1]. Upon hydrolysis, H_2O_2 is released along with two $Mn^{III}(Me_2XBC)\ (OH)_2^+$ ions. The free H_2O_2 oxidizes two more molecules of the Mn(II) complex, again possibly by formation of an –O–O– bridge. All four $Mn^{III}(Me_2XBC)(OH)_2^+$ ions then abstract hydrogen atoms from RH_2, or from RH, and are reduced back to their Mn(II) counterparts. For both iron(II) and cobalt(II), the obstacle of simple 1-electron oxidation by O_2, that derives from the low redox potential of the O_2/HO_2 couple, is commonly surmounted by substitution of a 2-electron process, or two closely coupled 1-electron events. Although peroxo-bridged transition metal complex dimers are commonly recognized in dioxygen activation in iron and cobalt chemistry [21], detailed mechanistic studies are needed for the present system.

The observation that the new manganese/Me_2XBC catalyst activates O_2 oxidations rekindled attempts to produce the corresponding hydrogen abstraction reaction using $Mn(Me_2EBC)Cl_2$. Under the identical conditions to those used for $Mn(Me_2XBC)Cl_2$, no oxidation is observed using $Mn(Me_2EBC)Cl_2$. Since the manganese(IV) complex of Me_2EBC is capable of hydrogen abstraction over a wide pH range [12d], it can also be concluded that oxygen activation of $Mn(Me_2EBC)Cl_2$ in basic solution does not produce the manganese(IV) species. In fact it is the manganese(III) complex that is produced and apparently, the manganese(III)/Me_2EBC system is incapable of hydrogen abstraction.

4. Conclusions

This work reports the synthesis of two *o*-xylylene cross-bridged cyclam ligands: 1,10,13,19-tetraazatricyclo[8.6.6.$0^{3,8}$]docosa-3,5,7-triene (H_2XBC), and its methylation product, 13,19-dimethyl-1,10,13,19-tetraazatricyclo[8.6.6.$0^{3,8}$]docosa-3,5,7-triene (Me_2XBC). Both ligands behave as true proton sponges and the synthesis of their Mn(II) and Fe(II) complexes requires strictly water-free reaction systems. The crystal structure of H_2XBC reveals a U-shaped conformation with a clearly defined cavity in which the four nitrogen atoms are oriented for metal complexation. The manganese(II) complex of Me_2XBC has been characterized and its structure determined. The parent H_2XBC complex exists as a dimer bridged by two chloride ions, while Me_2XBC forms the expected monomeric octahedral complex [Mn(Me_2XBC)Cl_2]. The Mn^{3+}/Mn^{2+} couple of the manganese(III) complex with Me_2XBC displayed an impressively high redox potential, indicating a promising oxidizing capability of this manganese(III) complex. The high potential of the Mn^{3+}/Mn^{2+} couple and the absence of any evidence for a Mn^{IV}complex with this ligand clearly show that Me_2XBC is less effective than Me_2EBC at stabilizing higher oxidation states of manganese. In buffered basic aqueous solution, Mn(Me_2XBC)Cl_2 activates dioxygen and catalyzes hydrogen abstraction from selected substrates. A possible mechanism is suggested for this oxygen activation and hydrogen abstraction process.

Supplementary data

Available in the on-line version.

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