Synthesis, structural studies, and oxidation catalysis of the manganese(II), iron(II), and copper(II) complexes of a 2-pyridylmethyl pendant armed side-bridged cyclam

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We have studied cross-bridged cyclam complexes of manganese and iron for nearly a decade and a half as oxidation catalysts [1–14]. The manganese complex of 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane [15] (M e E B C, Scheme 1) in particular, has a rich oxidation chemistry [5–14]. This compound, which we propose to call “the Busch catalyst”, was initially synthesized as an oxidation catalyst because the cross-bridged ligand could rigidly bind the oxygen-reactive manganese metal and stop it from being lost in the form of MnO2 [1–4]. Que has determined that the iron complex of Me E B C is an efficient olefin epoxidation catalyst with H2O2 oxidant under appropriate conditions as well [16]. (See Scheme 2.)

Cyclam ligands structurally reinforced with an ethylene bridge between nitrogens 1 and 4 (i.e. “side-bridged”) have been known since 1980 [17–26]. The additional bridge provides rigidity, configurational selectivity, and kinetic stability and has been synthetically put in place by several different methods [17–21]. Like other cyclam ligands, additional utility can be added by addition of pendant arms, which have included in Scheme 1, structure 1: R and/or R’ = H [17,21], Me [19], Et [20], Bz [19,23,22], Bz-p-NO2 [22,25], Bz-p-NH2 [22], CH2CO2H [24,26], CH2PO3H [25,26] and others.

An interesting 2-pyridylmethyltrimethylcyclam ligand (Scheme 1, structure 2) was reported by Que and coworkers [27] and stimulated our present work. Its iron complex activated dioxygen and formed an oxoiron(IV) intermediate that was crystallographically characterized, but has not been pursued further as a catalyst. [27] Although 2-pyridylmethyl pendant armed unbridged cyclams are ubiquitous [28–38], no 2-pyridylmethyl pendant armed side-bridged or cross-bridged cyclams had been reported prior to our work. Due to our experience with bridged cyclam oxidation catalysts, we set out to synthesize and characterize side- and cross-bridged cyclam ligands containing a 2-pyridylmethyl pendant arm, along with their most biologically relevant oxidation active metal ion complexes: manganese, iron, and copper. Our cross-bridged work has been reported elsewhere [39]. Here, we report on the results of our efforts with the side-bridged cyclam ligand, (Scheme 1, structure 3) and the screening of its complexes as potential oxidation catalysts.

Alkylation of the cyclam-glyoxal bisaminal 4 in typical Sn2 solvents like acetonitrile was unsuccessful due to self-reaction of the picolyl chloride. So, we explored the chlorinated solvents [40] to stabilize this
reagent in the presence of the bisaminal and found successful, although low-yielding, monoalkylation with picolyl chloride in chloroform at room temperature [41]. We raised the yields of the monoalkyl salt 5 to 66% by addition of KI and increasing the temperature to reflux over 6 days. Typical reduction conditions [23] gave 3 in good yield. Metal complexation with anhydrous metal chlorides in dry solvents under nitrogen gave adequate yields of the desired complexes [41].

The X-ray crystal structures of the H23Cl2•2H2O and [Cu(3)][PF6]2•C5H7O were obtained and are depicted in Fig. 1 [42]. The ligand is protonated at one of the piperazine tertiary nitrogens, and at the secondary nitrogen of the cyclam ring. There is an extensive hydrogen bonding network between the chloride anions, the two waters of crystallization, the cyclam nitrogens, and their protons. The pyridine nitrogen is oriented away from the center of the cyclam ring and is not involved in the hydrogen bonding network.

Upon coordination of Cu2+, the pyridine nitrogen is oriented into the center of the cyclam ring and coordinates the Cu2+ ion [43]. High spin n = 5 is consistent presence of one chloride in the elemental analysis of this complex led us to conclude that the most likely structure is a 6-coordinate pseudo-octahedral one. If the chloride is not coordinated and the complex is only 5-coordinate, precipitation by PF6 would have led to the di-hexafluorophosphate salt.

Perhaps the most interesting contribution to structural information came from the magnetic moment of [Fe(3)]Cl2, μ = 3.10 μB, which is most consistent with n = 2 for a low spin 5-coordinate d6 Fe2+ metal ion [44]. In our previous experience with Mn2+ and Fe2+ complexes of bridged tetraazamacrocycles [1,3,45], both ions agree in that they were high spin and 6-coordinate. However, in this case, Mn(3)Cl+ appears 6-coordinate and high spin, while Fe(3)2+ appears 5-coordinate and low spin. Two supporting pieces of evidence for this perhaps unexpected geometry for the Fe2+ complex are (1) the 5-coordinate Cu(3)2+ crystal structure presented above for this ligand system; and (2) an unpublished crystal structure in which Fe2+ is coordinated to the four nitrogens of a similar ethylene side-bridged ligand having a methyl group in place of the pyridylimethyl group of 3, and a chloro ligand [39]. Interestingly, a six-coordinate 1,8-bispyridylmethylcyclam Fe2+ complex with spin-crossover properties and a transition temperature to low spin of 150 K is known [46]. Of course, low spin d2 Fe2+ complexes are ubiquitous in organometallic chemistry. A number of 5-coordinate low-spin Fe2+ examples have been published [47–50].

In anticipation of carrying out oxidation studies, we obtained cyclic voltammograms (Fig. 2) on these complexes in acetonitrile looking for multiple stabilized oxidations states if catalytic processes were to be likely. Unfortunately, only one reversible redox wave was observed for each complex. Relative to SHE, Cu(3)2+ gave a reversible Cu1+/2+ redox wave at E1/2 = −0.586 V (ΔE = 77 mV). No oxidation to Cu3+ was observed, which is perhaps not surprising, as there are no negatively charged ligands to help stabilize the Cu3+ cation. Cu(Me2EBC)Cl+ has an irreversible Cu2+ to Cu3+ reuction wave at Ered = −0.544 V and an irreversible Cu2+ oxidation to Cu3+ at Eox = +1.530 V [51]. In comparison, Cu(3)2+ is more difficult to oxidize (due to lack of negatively charged ligands) and more reversibly reduced.

Mn(3)Cl+ gave a reversible Mn2+/3+ redox wave at E1/2 = +0.685 V (ΔE = 93 mV) and an irreversible reduction at Ered = −0.685 V. This can be compared to the well-known Mn(Me2EBC)Cl2 catalyst [1] which has reversible Mn2+/3+ and Mn3+/4+ waves at E1/2 = +0.585 V (ΔE = 61 mV) and E1/2 = +1.343 V (ΔE = 65 mV), respectively. The single chloro ligand allows only Mn3+ to be accessed for Mn(3)Cl+, and at a higher potential, since only one negatively charged chloro ligand is present to
stabilize the growing positive charge. Reduction is possible here, when not observed for Mn(MeEBC)Cl2, but not reversible, likely due to the loss of the chloro ligand upon reduction to Mn+. 5-Coordinate Fe(3)2+ exhibits a complex cyclic voltammogram with a reversible Fe2+/3+ wave at E1/2 = +0.456 V (ΔE = 78 mV), two irreversible reductions at Ered = −0.802 V and −1.671 V, respectively, and a large return oxidation at Eox = −0.252 V. A much simpler behavior is observed for Fe(MeEBC)Cl2, with only E1/2 = 0.110 (ΔE = 63 mV) observed for Fe2+/3+ [1]. Oxidation is obviously much easier for the latter complex, where two negatively charged chloro ligands stabilize the positive charge. Reduction is observed only for Fe(3)2+, where no negatively charged ligands inhibit it. The complex behavior of Fe(3)2+ after the initial reduction is the subject of ongoing study.

Finally, we present initial oxidation screening data on these complexes. As shown in Table 1, compared with its analog, Mn(MeEBC)Cl2 complex, the redox activities of Cu(3)2+ and Mn(3)Cl+ are quite poor. In sulfide oxidation using H2O2 as oxidant, while the Mn(MeEBC)Cl2 catalyst provided nearly complete conversion of thioanisole (99.8%) with 44.3% yield of sulfoxide and 46.5% of sulfone, the Cu(3)2+ and Mn(3)Cl+ complexes are almost inactive for sulfide oxidation. However, Fe(3)2+ demonstrated some activity, providing 9.7% yield of sulfoxide, and 2.9% of sulfone with 15.6% conversion. Similarly, in hydrogen abstraction from 1,4-cyclohexadiene, Mn(MeEBC)Cl2 gave 71.4% yield of benzene with 86.2% conversion, and Cu(3)2+ and Mn(3)Cl+ complexes were still...
inactive for benzene formation (~3% yields represent natural benzene content in commercial 1,4-cyclohexadiene). Again, Fe(3+) complexes showed promising results only in the hydrogen atom abstraction of 1,4-cyclohexadiene by Fe(3+)2+, which is consistent with another iron complex from the literature having a similar redox potential [55]. Future work will include expanding the range of oxidation reactions possible with this catalyst and determination of its oxidation catalysis mechanisms.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2015.07.002.

References


Table 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conversion %</th>
<th>Yield % sulfoxide</th>
<th>Yield % sulfone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(Me2EBC)Cl2</td>
<td>99.8</td>
<td>44.3</td>
<td>46.5</td>
</tr>
<tr>
<td>[Mn(3)Cl]2+</td>
<td>8.3</td>
<td>0.2</td>
<td>0.02</td>
</tr>
<tr>
<td>[Fe(3)]2+</td>
<td>15.6</td>
<td>9.7</td>
<td>2.9</td>
</tr>
<tr>
<td>[Cu(2)]2+</td>
<td>6.1</td>
<td>3.4</td>
<td>1.9</td>
</tr>
</tbody>
</table>

1:1 MeOH:H2O, 1,4-cyclohexadiene 0.05 M, complexes 1 mM, H2O2 0.02 ml, 303 K, 4 h

Complex | Conversion % | Yield % benzene |
---------|--------------|----------------|
Mn(Me2EBC)Cl2 | 86.2 | 71.4 |
[Mn(3)Cl]2+    | 23.1 | 3.5 |
[Fe(3)]2+      | 44.5 | 23.6 |
[Cu(2)]2+      | 29.6 | 4.0 |
6.059 g (0.160 mol, 5 eq.) of NaBH4 was added and the reaction was stirred at room temperature for 1 day during which the brown FeCl3 beads dissolved and formed a yellow precipitate. This product was filtered on a glass frit, washed with ether, and allowed to dry open to the atmosphere of the glovebox. A second crop was obtained from partial evaporation of the filtrate followed by filtration of the additional yellow powder that precipitated. Combined Yield = 0.275 g (82%). Electrospray mass spectrometry (in MeOH/H2O) gave a peak at m/z = 421 corresponding to (Fe3+OH2(OCH3)2)2+. Anal. Calc. for [Fe3(H2O)2(NH3)2][ClO4]•0.5H2O: C = 47.50, H 7.12, N 15.45, found C 47.58, H 7.46, N 15.31. [Mn3(Cl3)2][PF6] and [Cu3(Cl3)][PF6]: The general procedure for (Fe3+)Cl2 above was followed, however, these reactions gave little or no precipitation. The solutions were filtered to remove trace solids, which were discarded. The filtrates were then evaporated under vacuum to give crude [M(3)] chloride salts that was dissolved in a minimum MeOH in the glovebox. To these solutions were added 0.165 g (0.005 mol, 5 eq.) of NH4PF6 likewise dissolved in a minimum of MeOH. Precipitation of the PF6− salts products immediately, but the suspensions were allowed to stir approximately 1 h to complete precipitation. The solid products were filtered off, washed with diethyl ether, and allowed to dry overnight open to the glovebox atmosphere.[Mn3(Cl3)][PF6]: Yield = 0.395 g (71%) of white powder. Electrospray mass spectrometry gave peaks at m/z = 391 corresponding to (Mn3+H3O+)
 and m/z = 421 corresponding to (Mn3+Cl3(OH2)5).
 Anal. Calc. for [Mn3(Cl3)2(NH3)2][PF6]: C = 35.62, H 6.15, N 11.34; found C 35.62, H 6.10, N 11.67. [Cu3(Cl3)][PF6]: Yield = 0.457 g (68%) of blue powder. Electrospray mass spectrometry gave peaks at m/z = 379 corresponding to (Cu3+I)2− and m/z = 190 corresponding to (Cu3+I)2-. Anal. Calc. for [Cu3(H3O)2(NH3)2][PF6]: C = 20.35, H 4.69, N 10.32. X-ray quality crystals were obtained from the diffusion of ether into an acetone solution.


X-ray crystallographic details: Single crystal X-ray diffraction data were collected in series of o-scans using a Stoe IPDS image plate diffractometer utilizing monochromated Mo radiation (λ = 0.71073 Å). Standard procedures were employed for the integration and processing of the data using X-RED [53]. Samples were coated in a thin film of perchloroform oil and mounted at the tip of a glass fibre located on a goniometer. Data were collected from crystals held at 150 K in an Oxford Instruments nitrogen gas cryostream. Crystal structures were solved using routine automatic direct methods implemented within SHELXS-97 [54]. Completion of structure determination was achieved by performing least squares refinement against all unique F2 values using SHELXL-97 [54]. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed using a riding model. Where the location of hydrogen atoms was obvious from distance Fourier maps, C H bond lengths were refined subject to chemically sensible restraints.

Crystal Data for H[C18H31N5]Cl2•2H2O: C18H31N5Cl2•2H2O: Cu2C39H68N10OP4F24, Mr = 1399.99, Z = 4, T = 150(2) K, Monoclinic, P 21/c, a = 17.1554(16) Å, b = 10.8884(21) Å, c = 13.0825(11) Å, α = 90°, β = 100.33(2)°, γ = 90°, V = 2271.6(4) Å3, F(000) = 920, GOV = 0.822. A total of 12083 reflections were collected, of which 4630 were unique (Rint(1) = 0.0082), R1(1–2θ) = 0.0421, wR2 = 0.1297. Crystal Data for [(Cu3I3)]Cl2(OH)(OCH3): Cu3I3•(OH)(OCH3), Mr = 1399.79, Z = 4, T = 150(2) K, Orthorhombic, P c a 1, a = 17.6603(5) Å, b = 9.1845(5) Å, c = 31.3088(18) Å, α = 90°, β = 90°, γ = 90°, V = 5472.6(4) Å3, F(000) = 2856, GOV = 0.798. A total of 33224 reflections were collected, of which 9229 were unique (Rint(1) = 0.0554), R1(1–2θ) = 0.0318, wR2 = 0.0569.


