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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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ABSTRACT

The first 2-pyridylmethyl pendant armed structurally reinforced cyclam ligand has been synthesized and successfully complexed to Mn^{2+} , Fe^{2+} , and Cu^{2+} cations. X-ray crystal structures were obtained for the diprotonated ligand and its Cu^{2+} complex demonstrating pentadentate binding of the ligand with *trans-II* configuration of the side-bridged cyclam ring, leaving a potential labile binding site *cis* to the pyridine donor for interaction of the complex with oxidants and/or substrates. The electronic properties of these complexes were determined by means of solid state magnetic moment, with a low value of $\mu = 3.10 \,\mu_B$ for the Fe²⁺ complex suggesting that it has a trigonal bipyramidal coordination geometry, matching the crystal structure of the Cu^{2+} complex, while the $\mu = 5.52 \,\mu_B$ value for the Mn^{2+} complex suggests that it is high spin octahedral. Cyclic voltammetry in acetonitrile revealed reversible redox processes in all three complexes, suggesting that catalytic reactivity involving electron transfer processes are possible for these complexes. Screening for oxidation catalysis using hydrogen peroxide as the terminal oxidant identified the Fe²⁺ complex as the oxidation catalysts most worthy of continued development.

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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-1,4,8,11tetraazabicyclo[6.6.2]hexadecane [15] (**Me₂EBC**, 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 **Me₂EBC** 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 dioxogen and formed an oxoiron(IV) intermediate that was crystallographically characterized, but has not been pursued further as a catalyst. [27] Although 2pyridylmethyl pendant armed unbridged cyclams are ubiquitous [28-38], no 2-pyridylmethyl pendant armed side-bridged or crossbridged 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 2pyridylmethyl 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 $S_N 2$ solvents like acetonitrile was unsuccessful due to self-reaction of the picolyl chloride. So, we explored the chlorinated solvents [40] to stabilize this

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Scheme 1. Ligands discussed in this paper.

reagent in the presence of the bisaminal and found successful, although low-yielding, monoalykylation 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 $H_23Cl_2 \cdot 2 H_2O$ and $[Cu(3)][PF_6]_2 \cdot C_3H_6O$ 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 Cu^{2+} , the pyridine nitrogen is oriented into the center of the cyclam ring and coordinates the Cu²⁺ ion located there. This compound contains Cu²⁺ in two different coordination geometries. The ligand coordinates through each of the nitrogen atoms but in a slightly different orientation. The two copper complexes are approximately enantiomers, as shown in Fig. 1(c). The coordination geometry around the copper(II) ion is somewhat between trigonal bipyramidal (as shown in Fig. 1(b)) and square pyramidal (as shown in Fig. 1(c)). To illustrate the slight differences between the two different metal ion coordination geometries of this structure, square pyramidal type bond angles for the two different copper(II) ions are given: Cu(1) N-Cu-N angles/°: (in plane) 100.9(2), 74.0(2), 94.75(19), 87.79(19); (to N5) 82.91(17), 118.02(18), 101.94(17), 97.03(18). Cu(2) N-Cu-N angles/°: (in plane) 102.10(19), 73.4(2), 91.7(2), 86.2(2); (to N25) 80.5(2), 107.85(18), 107.37(19), 120.5(2). Complete metrical parameters for both structures are given in the Supplementary Information.

Unfortunately, crystal structures of the Mn^{2+} and Fe^{2+} complexes were not obtained. We sought other hints at their structures and turned to solid state magnetic moments to help determine them. First, the magnetic moment of $[Cu(3)][PF_6]_2$ was determined to be 2.32 μ_B , which is consistent with n = 1 for a d⁹ Cu²⁺ ion [43]. $[Mn(3)Cl]PF_6$ was determined to have $\mu = 5.52 \mu_B$, which is consistent with n = 5for a high spin octahedral d⁵ Mn^{2+} metal ion [43]. High spin n = 5 is not diagnostic of a particular coordination geometry for Mn^{2+} , but the consistent presence of one chloride in the elemental analysis of this complex led us to conclude that the most likely structure is a 6coordinate pseudo-octahedral one. If the chloride is not coordinated and the complex is only 5-coordinate, precipitation by PF_6^- would have led to the di-hexafluorophosphate salt.

Perhaps the most interesting contribution to structural information came from the magnetic moment of $[Fe(3)]Cl_2$. $\mu = 3.10 \mu_B$, which is most consistent with n = 2 for a low spin 5-coordinate $d^6 Fe^{2+}$ 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 Fe^{2+} 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 Fe^{2+} is coordinated to the four nitrogens of a similar ethylene side-bridged ligand having a methyl group in place of the pyridylmethyl 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 d⁶ Fe²⁺ complexes are ubiquitous in organometallic chemistry. A number of 5coordinate low-spin Fe^{2+} 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 Cu^{1+/2+} redox wave at $E_{1/2} = -0.586$ V ($\Delta E = 77$ 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 Cu⁺ reduction wave at $E_{red} = -0.544$ V and an irreversible Cu²⁺ oxidation to Cu³⁺ at $E_{ox} = +1.530$ 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 $Mn^{2+/3+}$ redox wave at $E_{1/2} = +0.856$ V ($\Delta E = 93$ mV) and an irreversible reduction at $E_{red} = -0.685$ V. This can be compared to the well-known $Mn(Me_2EBC)Cl_2$ catalyst [1] which has reversible $Mn^{2+/3+}$ and $Mn^{3+/4+}$ waves at $E_{1/2} = +0.585$ V ($\Delta E = 61$ mV) and $E_{1/2} = +1.343$ ($\Delta E = 65$ mV), respectively. The single chloro ligand allows only Mn^{3+} to be accessed for $Mn(3)Cl^+$, and at a higher potential, since only one negatively charged chloro ligand is present to



Scheme 2. Synthesis of 3. a) i. CHCl₃, 2 eq. picolyl chloride hydrochloride, 4 eq. NaHCO₃, 1 h, filter to remove solids; ii. 1 eq. of (1), 2 eq. KI, reflux 6 days; b) i. 95% EtOH, 5 eq. NaBH₄, N₂, reflux, 1.5 h; ii. 12 M HCl(aq), 30% KOH(aq), benzene extraction.



Fig. 1. (a) Structure of $H_23Cl_2 \cdot 2H_2O$, (b) structure of $Cu(3)^{2+}$ depicted as an approximate trigonal bipyramidal geometry and (c) structure of $Cu(3)^{2+}$ depicted as an approximate square-based pyramidal geometry and showing that the two slightly different ligand orientations are approximately enantiomers.

stabilize the growing positive charge. Reduction is possible here, when not observed for $Mn(Me_2EBC)Cl_2$, but not reversible, likely due to the loss of the chloro ligand upon reduction to Mn^+ .



Fig. 2. Cyclic voltammograms in acetonitrile vs. SHE for (a) $Cu(3)^{2+}$, (b) $Fe(3)^{2+}$, and (c) $Mn(3)Cl^+$.

5-Coordinate Fe(**3**)²⁺ exhibits a complex cyclic voltammogram with a reversible Fe^{2+/3+} wave at $E_{1/2} = +0.456$ V ($\Delta E = 78$ mV), two irreversible reductions at $E_{red} = -0.802$ V and -1.671 V, respectively, and a large return oxidation at $E_{ox} = -0.252$ V. A much simpler behavior is observed for Fe(**Me₂EBC**)Cl₂, with only $E_{1/2} = 0.110$ ($\Delta E = 63$ mV) observed for Fe^{2+/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, $Mn(Me_2EBC)Cl_2$ complex, the redox activities of $Cu(3)^{2+}$, and $Mn(3)Cl^+$ are quite poor. In sulfide oxidation using H_2O_2 as oxidant, while the $Mn(Me_2EBC)Cl_2$ 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, $Mn(Me_2EBC)Cl_2$ gave 71.4% yield of benzene with 86.2% conversion, and $Cu(3)^{2+}$ and $Mn(3)Cl^+$ complexes were still

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Table 1

Oxidation catalysis screening results for manganese(II), iron(II), and copper(II) complexes of 3, in comparison to Mn(Me2EBC)Cl2.

$ \begin{array}{c} & \overset{CH_3CN, \text{ thioanisole 0.1 M,}}{\underset{M_2O_2 \ 0.2 \ \text{mL}, \ 303 \ \text{K}, \ 6 \ \text{h}}} & \overset{O}{\underset{K}{\overset{S}{\overset{K}}}} & \overset{O}{\underset{K}{\overset{S}{\overset{K}}}} & \overset{O}{\underset{K}{\overset{S}{\overset{K}}}} & \overset{O}{\underset{K}{\overset{K}}} & \overset{O}{\underset{K}{\overset{K}{\overset{K}}}} & \overset{O}{\underset{K}{\overset{K}{\overset{K}}} & \overset{O}{\underset{K}{\overset{K}{\overset{K}}}} & \overset{O}{\overset{K}{\overset{K}}} & \overset{O}{\underset{K}{\overset{K}{\overset{K}}} & \overset{O}{\overset{K}} & \overset{O}{\overset{K}} & \overset{O}{\overset{K}} & \overset{O}{\overset{K}}} & \overset{O}{\overset{K}{\overset{K}{\overset{K}}}} & \overset{O}{\overset{K}{\overset{K}}} & \overset{O}{\overset{K}} & \overset{O}{\overset{K}} & \overset{O}{\overset{K}} & \overset{C}{\overset{K}} & \overset{O}{\overset{K}} & \overset{C}{\overset{K}}} & \overset{O}{\overset{K}} & \overset{C}{\overset{K}} & \overset{O}{\overset{K}} & \overset{C}{\overset{K}} & \overset{O}{\overset{K}} & \overset{O}{\overset{K}} & \overset{O}{\overset{K}} & \overset{O}{\overset{K}} & \overset{O}{\overset{K} & \overset{O}{\overset{K}} & \overset{O}{\overset{K}} & \overset{O}{\overset{K}} & \overset{O}{\overset{K} & \overset{O}{\overset{K}} & \overset{O}{\overset{K} & \overset{C}{\overset{K}} & \overset{O}{\overset{K} & \overset{C}{\overset{K}} & \overset{O}{\overset{K} & \overset{C}{\overset{K}} & \overset{O}{\overset{K} & \overset{C}{\overset{K}} & \overset{O}{\overset{K} & \overset{C}$			
Complex	Conversion %	Yield % sulfoxide	Yield % sulfone
Mn(Me₂EBC)Cl ₂	99.8	44.3	46.5
$[Mn(3)Cl]^+$	8.3	0.2	0.02
$[Fe(3)]^{2+}$	15.6	9.7	2.9
1:1 MeOH:H ₂ O, 1,4-cyclohexadiene 0.05 M, complexes 1 mM, $H_2O_2 0.02 \text{ mL}$, 303 K, 4 h			
Complex	Conversion %	Yield % benzene	
Mn(Me ₂ EBC)Cl ₂	86.2	71.4	
$[Mn(3)Cl]^+$	23.1	3.5	
$[Fe(3)]^{2+}$	44.5	23.6	
$[Cu(3)]^{2+}$	29.6	4	

inactive for benzene formation (~3% yields represent natural benzene content in commercial 1,4-cyclohexadiene). Again, $Fe(3)^{2+}$ provides more encouraging results, generating 23.6% yield of benzene with 44.5% conversion.

These results are perhaps not surprising, when reconciled with the electrochemical studies (Fig. 2). Mn(3)Cl⁺ has only a redox couple of $Mn^{2+/3+}$ at $E_{1/2} = +0.856$ V, which is much higher than that of the corresponding $Mn^{2+/3+}$ couple of $Mn(Me_2EBC)Cl_2$ ($E_{1/2}$ = +0.585 V), and no access to Mn(IV). Therefore, the catalytic cycle of the $Mn(3)Cl^+$ complex is very sluggish in oxidations. Similar sluggish redox behavior is observed in $Cu(3)^{2+}$ since its oxidation to $Cu(3)^{3+}$ is not observed. For the $Fe(3)^{2+}$ complex, although its catalytic activity in sulfide oxidation, an oxygen transfer process, is poor, it still demonstrates a relatively good activity in hydrogen abstraction because its redox couple for $Fe^{2+/3+}$ is modest ($E_{1/2} =$ +0.456 V) and even lower than that of Mn(Me₂EBC)Cl₂. Consistent with the hydrogen abstraction activity of the $Fe(3)^{2+}$ complex, Stack has reported [55] that $Fe(PY5)(OH)^{3+}$, which has a potential of $E_{pc} = +0.555$ V, is capable of stoichiometric hydrogen abstraction from 9,10-dihydroanthracene (PY5 = 2,6-bis-(bis(2pyridyl)methoxymethane)pyridine). This result encourages us to continue the exploration of the $Fe(3)^{2+}$ complex and its biological relevance to lipoxygenase [56] in the future.

In conclusion, a new pyridylmethyl N-pendant arm, side-bridged cyclam ligand, 3, has been synthesized, and its diprotonated salt structurally characterized, with a key synthetic step the use of non-polar chloroform to decrease the self-reactivity of picolyl chloride in the presence of bisaminal 4. Divalent Mn, Fe, and Cu complexes were synthesized and the copper(II) complex structurally characterized by X-ray crystallography as 5-coordinate $Cu(3)^{2+}$ showing the cyclam ring of **3** in a *trans*-II configuration and the chelated pyridine nitrogen bound to the Cu²⁺ ion. Solid state magnetic moment determination and elemental analysis revealed a high spin, octahedral Mn(3)Cl⁺ cation, but a 5-coordinate, low-spin $Fe(3)^{2+}$ cation. Electrochemical studies in acetonitrile revealed reversible access to only two oxidation states for each metal ion, whereas optimal behavior for successful oxidation catalysis is likely a greater redox range. Preliminary screens for oxidation catalysis using H₂O₂ as the oxidant carried out on all three 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.

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- [41] Synthetic details3a-(pyridin-2-ylmethyl)-decahydro-5a,8a,10a-triaaza-3a-azoniapyrenium iodide (5). 13. g (0.08096 mol, 2 eq.) of picolyl chloride hydrochloride and 13.60 g (0.1619 mol, 4 eq.) of anhydrous NaHCO3 were stirred in 700 ml of chloroform for 1 h. Solids were removed by filtration and the filtrate was added to 9.00 g (0.04048 mol, 1 eq.) of (4) [52] and 13.44 g (0.08096 mol, 2 eq.) of KI. The reaction was stirred and heated to reflux for 6 d under nitrogen, during which it became an orange color. After cooling, minimal solids were removed by filtration and discarded. The filtrate was evaporated to 100 ml volume and excess diethyl ether was added to precipitate the yellow solid product, which was filtered on a glass frit, washed with diethyl ether, and dried under vacuum. Yield = 11.841 g (66%). Electrospray mass spectrometry gave a single peak at m/z = 314 corresponding to $(M-I)^+$. Anal. Calc. for C₁₈H₂₈N₅I •H₂O: C 47.06, H 6.58, N 15.25; found: C 46.87, H 6.54, N 14.88. ¹H NMR (300 MHz, CDCl₃) δ 1.36 (d, 1H), 1.84 (d, 1H), 2.25 (m, 2H), 2.41 (d, 1H), 2.56 (d, 1H), 2.66 (m, 2H), 3.03 (m, 6H), 3.23 (t, 1H), 3.65 (m, 2H), 3.89 (d, 1H), 4.21 (m, 2H), 4.40 (td, 1H), 4.58 (s, 1H), 5.45 (m, 2H), 7.41 (m, 1H), 7.84 (m, 1H), 8.31 (d, 1H), 8.66 (d, 1H). ¹³C{¹H} NMR (75.6 MHz, D₂O) δ 18.0, 18.4, 41.9, 46.6, 49.4, 51.3, 51.9, 53.2, 54.0, 60.5, 62.9, 69.5, 82.2, 125.8, 129.0, 138.6, 146.6, 150.3.5-(pyridin-2-ylmethyl)-1,5,8,12-tetraazabicyclo[10.2.2]hexadecane (3). 14.138 g (0.0320 mol, 1 eq.) of 5 was stirred in 1 L of 95% EtOH in a 2 L roundbottom flask. 6.059 g (0.160 mol, 5 eq.) of NaBH₄ was added and the reaction was stirred at reflux for 1.5 h under N₂. Upon cooling, 12 M HCl was added to a pH of 2. Solvent was removed under vacuum and the residue was dissolved in 100 ml of water to which 200 ml of 30% KOH was added. The cloudy white suspension was extracted into benzene, dried over Na_2SO_4 , and evaporated to a tan oil. Yield = 7.947 g (78%). Electrospray mass spectrometry gave a single peak at m/z = 318 corresponding to (MH)⁺. Anal. Calc. for C₁₈H₃₁N₅ •1.3H₂O •0.1C₆H₆: C 64.07, H 9.89, N 20.08; found: C 63.80, H 10.00, N 19.87. ¹H NMR (300 MHz, CDCl₃) δ 1.65 (m, 4H), 2.16 (m, 2H), 2.45-2.65 (m, 11H), 2.86 (m, 4H), 3.14 (m, 2H), 3.73 (s, 2H), 3.82 (m, 2H), 7.09 (m, 1H), 7.30 (t, 1H), 7.56 (t, 1H), 8.45 (d, 1H). ¹³C(¹H) MMR (75.6 MHz, D₂O) δ 23.5, 26.1, 48.0, 48.1, 50.4, 51.0, 55.0, 55.1, 55.7, 56.9, 58.9, 121.8, 123.6, 135.9, 148.9, 159.1. X-ray quality crystals of the diprotonated salt H₂2²⁺ were grown from evaporation of the acetonitrile solvent from a complexation reaction of **3** with FeCl₂ which yielded, in addition to the complex product, a small amount of colorless crystals of H₂3Cl₂ •2 H₂O.[Fe(3)]Cl₂: 0.317 g (0.001 mol) of (3) and 0.127 g anhydrous FeCl₂ were added to 10 ml of anhydrous acetonitrile in an inert atmosphere glovebox. The

reaction was stirred at room temperature for 1 day during which the brown FeCl₂ beads dissolved and formed a vellow 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 (62%). Electrospray mass spectrometry (in MeOH/H₂O) gave a peak at m/z = 421 corresponding to $(Fe(3)(OH)(OH_3))^{2+}$. Anal. Calc. for $[Fe(C_{18}H_{31}N_5)]Cl_2 \bullet 0.5 H_2O: C 47.70, H 7.12, N 15.45; found C 47.58, H 7.46, N$ 15.31.[Mn(**3**)Cl]PF₆ and [Cu(**3**)][PF₆]₂: The general procedure for [Fe(**3** $)]Cl_2$ 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 0.815 g (0.005 mol, 5 eq.) of NH₄PF₆ likewise dissolved in a minimum of MeOH. Precipitation of the PF₆ salt products was immediate, 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.[Mn(3)Cl]PF₆: Yield = 0.393 g (71%) of white powder. Electrospray mass spectrometry gave peaks at m/z = 393 corresponding to $Mn(3)(H_2O)^+$ and m/z = 421 corresponding to $(Mn(3)(CH_3OH)(H_2O)^+)$. Anal. Calc. for [Mn(C18H31N5)Cl]PF6 •3 H2O: C 35.62, H 6.15, N 11.54; found C 35.62, H 6.10, N 11.67.[Cu(3)][PF₆]₂ Yield = 0.457 g (68%) of blue powder. Electrospray mass spectrometry gave peaks at m/z = 379 corresponding to $(Cu(3))^+$ and m/z = 190 corresponding to $(Cu(3))^{2+}$. Anal. Calc. for $[Cu(C_{18}H_{31}N_5)][PF_6]_2$ •0.2 H₂O: C 32.05, H 4.69, N 10.38; found C 31.69, H 4.66, N 10.32. X-ray quality crystals were obtained from the diffusion of ether into an acetone solution.

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- [43] X-ray crystallographic details: Single crystal X-ray diffraction data were collected in series of ω -scans using a Stoe IPSD2 image plate diffractometer utilising monochromated Mo radiation ($\lambda = 0.71073$ 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 perfluoropolyether 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 structures 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 difference Fourier maps, C H bond lengths were refined subject to chemically sensible restraints.Crystal Data for H_2 **3** Cl_2 •2 H_2 O: $C_{18}H_{37}N_5Cl_2O_2$, $M_r = 426.42$, Z = 4, T =150(2) K, Monoclinic, P $2_1/c$, a = 17.1551(16) Å, b = 10.2884(11) Å, c = 13.0825(11) Å, $\alpha = 90^{\circ}$, $\beta = 100.328(7)^{\circ}$, $\gamma = 90^{\circ}$, V = 2271.6(4) Å³, F(000) = 920, GOF = 0.822. A total of 12083 reflections were collected, of which 4630 were unique ((R(int)) = 0.0828). R₁ (I > 2σ (I)) = 0.0421, wR2 = 0.1297. Crystal Data for $[Cu(3)][PF_6]_2 \cdot C_3H_6O$: $Cu_2C_{39}H_{68}N_{10}OP_4F_{24}$, $M_r = 1399.99$, Z = 4, T =150(2) K, Orthorhombic, P c a 21, a = 17.6639(8) Å, b = 9.8148(5) Å, c = 31.3088(18) Å, $\alpha = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 90^{\circ}$, V = 5427.6(4) Å³, F(000) = 2856, GOF = 0.798. A total of 33224 reflections were collected, of which 9229 were unique ((R(int)) = 0.0554). R_1 (I > 2 σ (I)) = 0.0318, wR2 = 0.0569.
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