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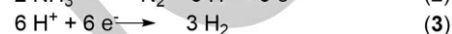
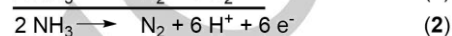
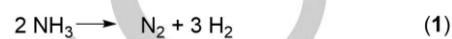
Towards Catalytic Ammonia Oxidation to Dinitrogen: A Synthetic Cycle Using a Simple Manganese Complex

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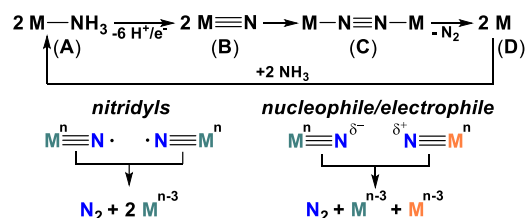
Abstract: Oxidation of the nucleophilic nitride, (salen)Mn≡N (**1**) with stoichiometric [Ar₃N][X] initiates a nitride coupling reaction to N₂, a major step toward catalytic ammonia oxidation (salen = *N,N*-bis(salicylidene)-ethylenediamine dianion; Ar = *p*-bromophenyl; X = [SbCl₆⁻] or [B(C₆F₅)₄⁻]). N₂ production was confirmed by mass spectral analysis of the isotopomer, **1-¹⁵N**, and the gas quantified. The metal products of oxidation were the reduced Mn^{III} dimers, [(salen)MnCl]₂ (**2**) or [(salen)Mn(OEt₂)₂][B(C₆F₅)₄]₂ (**3**) for X = [SbCl₆⁻] or [B(C₆F₅)₄⁻], respectively. The mechanism of nitride coupling was probed to distinguish a nitridyl from a nucleophilic/electrophilic coupling sequence. During these studies, a rare mixed-valent Mn^V/Mn^{III} bridging nitride, [(salen)Mn^V(μ-N)Mn^{III}(salen)][B(C₆F₅)₄]₂ (**4**), was isolated and its oxidation state assignment confirmed by X-Ray diffraction (XRD) studies, perpendicular and parallel-mode EPR and UV-Vis-NIR spectroscopies, as well as SQUID magnetometry. We found that **4** could subsequently be oxidized to **3**. Furthermore, in view of generating a catalytic system, **2** can be re-oxidized to **1** in the presence of NH₃ and NaOCl closing a pseudo-catalytic “synthetic” cycle. Together, the reduction of **1**→**2** followed by oxidation of **2**→**1** yield a genuine synthetic cycle for NH₃ oxidation, paving the way to the development of a fully catalytic system using abundant metal catalysis.

Renewable energy production is rapidly growing; however, with it will come an increased demand for new energy storage technologies. Up to 100 times more energy can be stored in chemical bonds than today’s batteries making them an ideal platform for storage and delivery (50-140 MJ/kg vs. ~0.5-1 MJ/kg).^[1] Hydrogen has a high gravimetric energy density (143 MJ/kg); however, handling and storing it remains a high barrier to implementing it as our primary energy currency. This problem can be overcome by the Haber-Bosch (HB) process to produce NH₃, an efficient H₂ storage reaction. With its high capacity (17.6 % wt. H₂), low cost (~\$1.5/kg H₂), ease of handling (-33 °C b.p.), and established production/distribution infrastructures (>

120 Mt/year), NH₃ is ideal for storing H₂.^[2] Furthermore, the energy loss of the HB process (1.5 GJ/t) is also easily countered by that stored in NH₃ (28.4 GJ/t).^[2]



Splitting NH₃ to N₂/H₂ under mild conditions is of particular interest in catalysis science today (eq. 1).^[2a, 2b] While electrochemical and heterogeneous systems have shown promise,^[3] homogeneous systems may provide a molecular-level probe to understanding the mechanism of the 6 e⁻ oxidation of NH₃ (eq. 2), key to overall splitting. While this strategy has been extensively used for N₂ reduction chemistry,^[4] NH₃ oxidation using well-defined metal complexes remains far less explored. Metal complexes of Mn,^[5] Co,^[6] Mo,^[7] Ru,^[8] and Os^[9] among others,^[10] have been used to oxidize NH₃ chemically or electrochemically to metal-nitride, dimetallic μ-N₂, or N₂ (**A**→**B**, **A**→**C** or **A**→**D**, respectively, Scheme 1, top). For the latter N–N bond formation pathways, intermediate metal-nitride coupling (**B**→**C**) – either through proposed bimolecular nitridyl^[11] (M≡N•) or nucleophilic (M≡N^{δ-}) + electrophilic (M≡N^{δ+}) coupling^[12] (Scheme 1, bottom) – is proposed as the main pathway to μ-N₂ or N₂ formation. Other nitrides, generated by N-atom transfer chemistry (ex. N₃⁻ photolysis), have also shown similar coupling behavior.^[11a, 11b, 12-13] While significant progress has been made towards NH₃ oxidation to various products (**B**, **C**, **D**), closing the cycle in a fully catalytic or pseudo-catalytic “synthetic” cycle,^[14] is rare.^[5c] Herein, we report a complete synthetic cycle for NH₃ oxidation at an abundant first-row metal complex of Mn. Preliminary mechanistic investigations into the coupling pathway (Scheme 1, bottom) are also reported.



Scheme 1. Top: reported conversions of NH₃ to N₂. Bottom: proposed mechanisms for nitride coupling to N₂.

The known nucleophilic Mn^V-nitride, (salen)Mn≡N (**1**), generated through NH₃ oxidation with NaOCl,^[5b] represents the first step of a potential synthetic cycle (**A**→**B**, Scheme 1, top and Fig. 1). We were interested in determining if chemical oxidation of **1** to **1**⁺ would induce nitride radical character (nitridyl) or render it electrophilic and susceptible to nucleophilic attack by

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an equivalent of **1** (Scheme 1, bottom).^[11a, 12] Electrochemical analysis of **1** using cyclic voltammetry in DCM revealed a quasi-reversible oxidation event at 0.53 V relative to the Fc/Fc⁺ (Fc = ferrocene) couple (Fig. 1 (right)), accessible using the known commercially available oxidant, [Ar₃N][SbCl₆] (Ar = *p*-bromophenyl; E^o = 0.70 V vs. Fc/Fc⁺).^[15] Oxidation of **1** with [Ar₃N][SbCl₆] in fluorobenzene (FB) resulted in loss of the diamagnetic signals of **1** and concomitant appearance of the aromatic NAr₃ signals in the ¹H NMR spectrum. A major paramagnetic product was subsequently isolated and crystallized by vapor diffusion of MeCN/Et₂O to yield single crystals suitable for XRD studies. The solid state structure revealed loss of the nitride with concurrent chloride capture, presumably from [SbCl₆], to yield the known^[16] Mn^{III} dimer [(salen)MnCl]₂ (**2**) in 82% yield. Similarly, treatment of **1** to 1 eq. of the non-coordinating oxidant, [Ar₃N][B(C₆F₅)₄],^[17] in FB again resulted in replacement of the diamagnetic peaks of **1** for a set of 3 paramagnetically shifted resonances at -8.7, -28.2, and -32.2 ppm in the ¹H NMR spectrum. Separation of NAr₃ from the reaction mixture resulted in the isolation of the paramagnetic product in 80% yield which was identified by single crystal XRD studies^[18] as the Et₂O-ligated Mn^{III} dimer, [(salen)Mn(OEt₂)₂][B(C₆F₅)₄]₂ (**3**; Fig. S1), similar to previously reported (salen)Mn^{III} complexes.^[19] Evans' method measurements of the spin state of **3** in MeCN-d₃ revealed an S = 2 spin state assuming a monomeric species in solution.^[20]

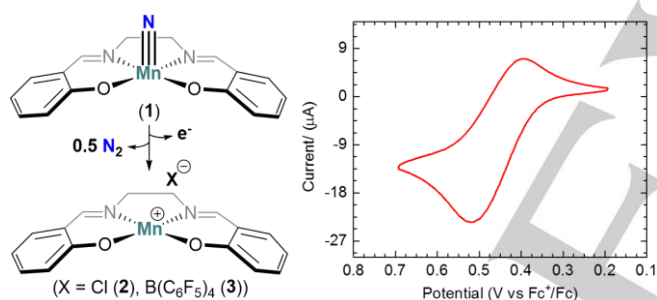
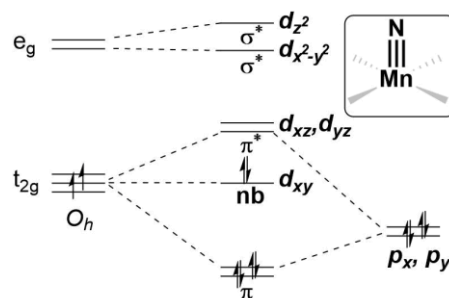


Figure 1. Left: oxidation of **1** with [Ar₃N][X] to yield **2** (X = Cl) or **3** (X = B(C₆F₅)₄) (monomeric forms are shown for simplicity). Right: cyclic voltammogram of **1** (1.0 mM) with 0.1 M [Bu₄N][PF₆] electrolyte in DCM (glassy C working electrode, scan rate 100 mV/s, referenced to Fc/Fc⁺).

The oxidation-initiated reduction of **1** → **2** or **1** → **3** resulted in loss of nitride and subsequent 3 e⁻ metal reduction via an intermediate **1**⁺ to Mn^{III} (**2** or **3**). As observed in other systems, such metal-nitride reduction is typically accompanied by N₂ generation.^[11a, 11b, 13d] In order to unambiguously confirm this here, we isotopically enriched the nitride in **1** to **1**-¹⁵N using ¹⁵NH₃ in the initial synthesis.^[5b, 21] The Mn≡N stretching frequency shifts from 1046 cm⁻¹ to 1018 cm⁻¹ in the IR spectrum for the ¹⁴N and ¹⁵N isotopomers, respectively. The headspace gas of an oxidation reaction (**1** → **3**) performed under Ar was sampled and analyzed by GC-MS using a gastight syringe. The presence of 27.5 % ¹⁵N₂ relative to background ¹⁴N₂, marked a significant deviation from natural abundance (0.13 % ¹⁵N₂ vs.

¹⁴N₂) (Fig. S2a). Similar to other reports,^[5c, 11a] we were unable to completely eliminate ¹⁴N₂ from the background. Treatment of a 1:1 mixture of **1**:**1**-¹⁵N to an equivalent of oxidant also resulted in the appearance of the mixed isotopomer ¹⁴N¹⁵N, in addition to ¹⁵N₂, in an approximate 2:1 ratio (19 % and 9.1 %, respectively), confirming the expected bimolecular coupling sequence (Fig. S2b). Similar results were obtained for the **1** → **2** conversion (Fig. S3). A related paper by Lau and co-workers described a similar reaction involving N₂ production (and in some cases NH₃) from Mn^V-imido (Mn=NR) intermediates generated through electrophilic conversion of related Mn^V-nitrides (similar to **1**).^[22] In addition, during the preparation of this manuscript, Clarke and Storr reported the analogous nitride coupling with related bulkier salen-type Mn-nitride species, observing in most cases nitride coupling to N₂.^[5c] In both ours and Storr's cases, oxidation of the Mn-nitride precursors is key to initiating nitride coupling to N₂, as opposed to imide coupling proposed by Lau.^[22]

Next, we were interested in probing the coupling pathway at play (nitridyl vs. nucleophilic/electrophilic – Scheme 1, bottom). With the pseudo-square pyramidal geometry and π orbital overlap between Mn and the nitride in **1**, oxidation of **1** should remove an electron from the non-bonding *d_{xy}* orbital (Scheme 2) as seen in similar complexes.^[5c, 23] Given the locus of orbital oxidation (*d_{xy}*) bears no π or π* contributions, we wanted to probe if the nitride in **1**⁺ would have electrophilic or radical character. It is worth noting that should the nucleophilic/electrophilic mechanism be at play, only half an equivalent of oxidant – oxidizing 0.5 eq. of **1** to **1**⁺ for subsequent reaction with 0.5 eq. of nucleophilic **1** – would be required for full conversion of all nitrides to N₂ (Scheme 1, bottom). To test this, we treated **1** to 0.5 eq. of [Ar₃N][B(C₆F₅)₄] in FB. Separation of NAr₃ from the reaction mixture resulted in the isolation of a red, MeCN-soluble, ¹H NMR-silent fraction. The complex was crystallized by vapor diffusion of a FB:DCM mixture in 40 % yield and identified by XRD studies as the bridged species, [(salen)Mn^V(μ-N)Mn^{III}(salen)][B(C₆F₅)₄] (**4**) (Fig. 2). The mixed-valency was assigned based on crystallographic, magnetometric, and spectroscopic analyses.



Scheme 2. Qualitative partial MO diagram for **1**.

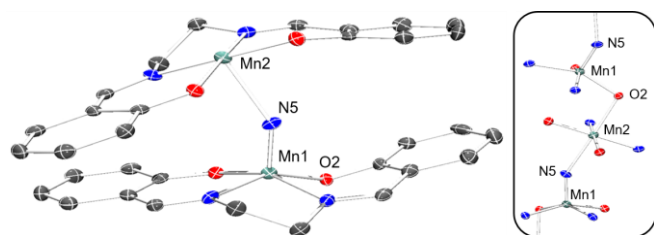


Figure 2. Solid-state structure of **4** with $[\text{B}(\text{C}_6\text{F}_5)_4]$ and H atoms omitted for clarity (Mn, teal; N, blue; O, red; C, black). Inset: the truncated 1-D chain of **4**. Pertinent bond lengths (Å) and angles ($^\circ$): Mn1–N5 (1.550(7)), Mn2–N5 (2.419(3)), Mn2–O2 (2.276(3)), Mn1–N5–Mn2 (149.4(2)), N5–Mn2–O2 (175.20(11)).

The solid-state structure of **4** reveals a Mn1–N5 bond length of 1.550(3) Å with a Mn center puckered out of the plane of the salen ligand by 0.440(3) Å consistent with a slightly elongated Mn≡N triple bond (Mn≡N = 1.512 Å and 0.451(1) Å out of plane Mn in **1**).^[5b] In contrast, the Mn2 center sits mostly in the plane of the salen ligand (out of plane by 0.071(2) Å) flanked at the apical site by N5 to form an elongated Mn2–N5 bond of 2.419(3) Å. In addition to these bonds, the cations of **4** form an infinite 1-D chain,^[24] wherein Mn2 also connects at the other axial site to O2 (2.276(3) Å) from the neighboring Mn^V-nitride bound salen (Fig. 2 box). The long Mn2–O2 and Mn2–N5 linkages are consistent with a Jahn-Teller distorted Mn^{III} center in a pseudo-octahedral field.^[24]

To gain further insight into the electronic structure of **4**, we collected variable temperature magnetic susceptibility ($\chi_M T$) and low temperature magnetization data (Fig. 3a). The $\chi_M T$ data collected at 0.5 T remains almost constant going from 3.16 to 3.31 $\text{cm}^3\text{K/mol}$ when scanned from 30 to 300 K, respectively. This is in agreement with the spin-only value of an ideal $S = 2$ (3.0 $\text{cm}^3\text{K/mol}$) system. Similarly, magnetization data at low temperature indicates the effect of zero-field splitting since data at 2 K and 5 T saturates at 3.12 μ_B , which is lower than the ideal value of $M = gS$ of 4 μ_B for an $S = 2$ (Fig. 3a, inset). Both $\chi_M T$ and reduced magnetization data were fit well to an $S = 2$ (red and black continuous lines in Fig. 3a), as described in the SI. The $\chi_M T$ fit parameters that best describe the data are: $g = 2.04$ and $\text{TIP} = 5.1 \times 10^{-4} \text{ cm}^3\text{mol}^{-1}$; while for the reduced magnetization data we obtained: $g = 2.42$ and $D = -8.5 \text{ cm}^{-1}$, where D corresponds to the axial zero-field splitting parameter.

The $S = 2$ assignment for **4** is further supported by X-band EPR measurements. We analyzed **4** by perpendicular- and parallel-mode EPR spectroscopy in MeCN at 6 K (Fig. 3b, inset). The perpendicular-mode spectrum was featureless as expected for an integer spin system, whereas the parallel-mode spectrum displayed a characteristic signal at $g = 7.84$, indicative of a high-spin ($S = 2$) Mn^{III} center.^[25] Lastly, the extent of redox localization was probed by UV-Vis-NIR (NIR = near-IR) spectroscopy (Fig. 3b). Intervalence charge transfer (IVCT) bands in the NIR appear due to inner-sphere electron charge transfer (thermally or photoinduced) between mixed-valent species. Three categories are used to describe the degree of communication: Class I equates to localized redox states with no

interaction between redox-sites; Class II corresponds to a partially delocalized mixed-valent state, and; Class III describes a fully delocalized redox state.^[26] The lack of an IVCT band in the NIR spectrum of **4** between 800–3300 nm (Fig. 3b) is consistent with a Class 1 assignment, with a localized ($S = 2$) Mn^{III} center and a diamagnetic ($S = 0$) Mn^V center (similar to the diamagnetism observed in **1**).^[5b] Collectively, these data support our mixed-valent oxidation state assignment with a localized high-spin Mn^{III} bridged to a diamagnetic Mn^V nitride center.

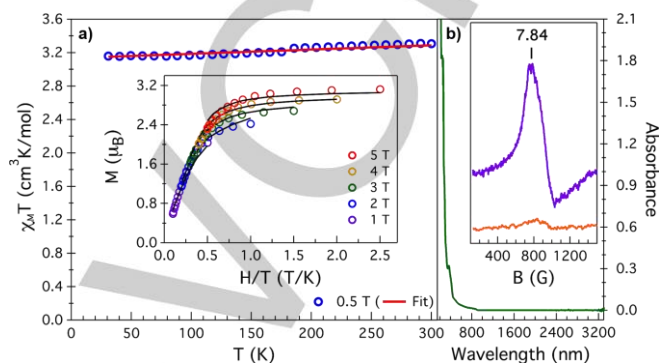
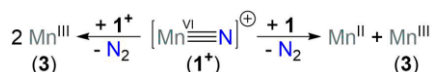


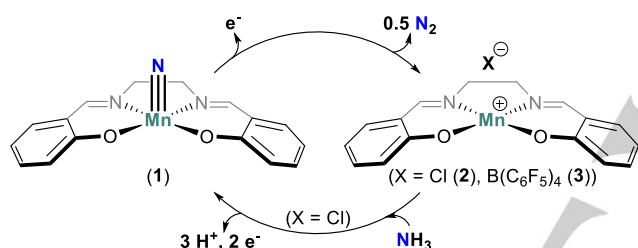
Figure 3. a) Variable temperature magnetic susceptibility measurements of **4** collected at 0.5 T (blue circles). Inset: Variable temperature, variable field magnetization data collected from 2–10 K with fields from 1–5 T. b) UV-Vis-NIR of **4** in MeCN (green). Inset: X-Band EPR spectra of **4** taken at 6 K in both perpendicular (orange) and parallel-modes (purple).

The conversion of **1** to **4** with 0.5 eq. of oxidant suggests that a nucleophilic/electrophilic coupling pathway is not at play here (Scheme 1, bottom). Such a coupling would not be expected to produce **4** and instead would involve **1**⁺ reacting with **1**, resulting in complete nitride conversion to N_2 , as well as generation of (salen)Mn^{II} and **3** (Scheme 3, right). Low valent Mn^{II} production was observed in Lau's report of Mn^V-imido coupling to generate N_2 (*vide supra*).^[22] To further probe this, a reaction mixture of **1** and 0.5 eq. of $[\text{Ar}_3\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ in MeCN was analyzed by perpendicular-mode EPR spectroscopy and compared to an authentic sample of the known (salen)Mn^{II} starting material. Whereas the latter displayed a broad isotropic feature at $g = 2.1$ consistent with literature reports,^[27] the former was featureless precluding the formation of any Mn^{II} by-products (Fig. S4). These experimental results support Storr's DFT calculations suggesting that significant nitridyl character in **1**⁺ (and similar species) may be expected and are likely operational in this coupling.^[5c] With this, we believe that production of **4** is the result of a bimolecular coupling of two nitridyls (**1**⁺) to generate **3** (Scheme 3, left) which rapidly react with the remaining **1** in solution to generate **4**. Lastly, we investigated whether **4** could be further oxidized to generate 2 equivalents of **3**. The CV of **4** displays a cathodically shifted oxidation event (relative to **1** – Fig. 1) at +0.43 V (Fig. S5), which is again accessible using the $[\text{Ar}_3\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ oxidant. Addition of 1.0 eq. of oxidant to a solution of **4** in MeCN- d_3 results in the immediate formation of the paramagnetically shifted resonances of **3** in the ¹H NMR spectrum, confirming that **4** is only an accessible intermediate in the conversion of **1**→**3**.



Scheme 3. Proposed coupling pathways (salen and anions omitted for simplicity).

As part of our endeavor to generate a catalytic system for NH_3 oxidation to N_2 , we turned to our initial results for the conversion of **1**→**2** (Fig. 1, left). While the oxidants, $[\text{Ar}_3\text{N}][\text{X}]$ ($\text{X} = \text{SbCl}_6, \text{B}(\text{C}_6\text{F}_5)_4$), are incompatible with NH_3 , **2** may be re-oxidized to **1** using NH_3 and NaOCl following a literature procedure,^[28] effectively closing the synthetic cycle, **D**→**B** (Scheme 1, top; Scheme 4). We performed several large scale oxidations of **1** using $[\text{Ar}_3\text{N}][\text{SbCl}_6]$, quantified the gas evolved, and found the reactions to produce between 70–84% N_2 within 10 minutes of mixing. Furthermore, removal of the solvent, followed by treatment with NH_3/NaOCl in a $\text{DCM}:\text{MeOH}$ solvent mixture, followed by purification,^[28] resulted in the isolation of pure **1** in varying yields from 50–63%. This represents a closed synthetic cycle for NH_3 oxidation (Scheme 4) and is to our knowledge the first example using an abundant metal.



Scheme 4.

In summary, we have described the oxidation-initiated $6 e^-$ reductive nitride coupling reaction to N_2 at Mn, including the experimental elucidation of the likely nitridyl coupling pathway, in support of previous theoretical work.^[5c] Isolation of a rare mixed valent $\text{Mn}^{\text{III}}/\text{Mn}^{\text{V}}$ intermediate, including full characterization of the mixed redox state, was also described. The reduced Mn species can be further oxidized with NH_3 and oxidant, closing the synthetic cycle for NH_3 oxidation. Further studies on this and related systems to generate a truly catalytic cycle, both chemically and/or electrochemically, are currently in progress in our lab.

Acknowledgements

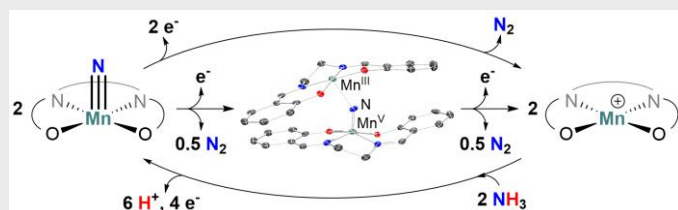
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Keywords: ammonia oxidation • hydrogen storage • nitride coupling • mixed-valent manganese • synthetic cycle

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Towards Catalytic Ammonia
Oxidation to Dinitrogen: A Synthetic
Cycle Using a Simple Manganese
Complex

Store that H₂! Oxidation of a simple (salen)Mn≡N results in the 6 e⁻ nitride coupling reaction, central to NH₃ oxidation to N₂. A complete synthetic cycle is established with implications for catalytic NH₃ oxidation for H₂ storage applications. An unusual mixed-valent Mn^V-Mn^{III} species is also isolated and characterized.