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Electronic structure of manganese complexes of the redox-non-innocent tetrazene ligand and evidence for the metal-azide/imido cycloaddition intermediate.

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Abstract: The first synthetic manganese tetrazene complexes are described as a redox pair comprising anionic [Mn[NuAd]3]− (1) and neutral Mn(NuAd)2 (2) complexes (NuAd = [Ad-N=N=N-N-Ad]−). Compound 1 is obtained in two forms as lithium salts, one as a catiionic Li3Mn cluster, and one as a Mn-Li 1-D ionic polymer. 1 is electronically described as a Mn(III) center with two [NuAd]− ligands. The one-electron oxidized 2 is crystalized in two morphologies, one as pure 2 and one as an acetonitrile adduct. Despite similar composition, the behavior of 2 differs in the two morphologies. Compound 2-MeCN is relatively air- and temperature-stable. Crystalline 2, on the other hand, exhibits a compositional, dynamic disorder wherein the tetrazene metallacycle ring-opens into a metal imide/azide complex detectable by X-ray crystallography and FTIR spectroscopy. Electronic structure of 2 has been examined by EPR and XPS spectroscopies and DFT calculations, which indicate 2 is best described as a Mn(III) ion with an anion radical delocalized across the two ligands through spin-polarization effects.

Introduction

The chemistry of oligonitrogen compounds is of fundamental interest to inorganic and theoretical chemists as nitrogen in its neutral form has the ability to form up to three bonds to its neighbors, and thus give networks and chains of nitrogen atoms. Numerous experimental and theoretical studies have explored the possibility of new nitrogen allotropes.[1] Oligonitrogen compounds such as azides,[2] azoles,[3] tetrazenes[4] and hexazenes[5] are of interest as topics of study in the inorganic chemistry of nitrogen, and have interdisciplinary appeal in the area of explosives and propellants,[6] as these compounds generally are exothermic in their decomposition, giving stable, expansive N2 gas as the primary decomposition product. Polymorphic forms of compounds are also of interest as crystal morphology has a significant effect on materials properties even for the same molecule.[7]

In particular, the tetrazene molecule has garnered some attention in nitrogen chemistry in its pure form[8] and as the nucleus of N-rich tetrazene derivatives,[40] including so-called “tetrazene explosive” or “tetracene”[9] used in priming formulations. But most frequently, tetrazene has been studied as a ligand for transition metals. Numerous metal complexes of tetrazene are known, almost all of them being 1:1 metal:tetrazene complexes,[10] with 1:2 complexes being rare, limited, to our knowledge, to a single structurally characterized example of a nickel bis(tetrazene) complex.[11] Metal tetrazenes are usually prepared from the reaction of a metal precursor with two equivalents of organic azide. The first azide is generally assumed to liberate N2, oxidizing the metal and generating a metal-imido complex, and the second azide undergoes a cycloaddition with the metal-imido complex to generate the metal(tetrazene) complex:[10a,b]

\[
\begin{align*}
M^{n+} + RN_2 & \rightarrow RN = M^{2+} + N_2 \quad (1) \\
RN = M^{2+} + RN & \rightarrow (RN)_2M^{2+} \quad (2)
\end{align*}
\]

This is generally assumed to be the mechanism of formation in most cases and has been experimentally supported[10c, 10d] Tetracentzene species have recently been implicated as nitrene transfer agents in contrast to the more traditionally cited metal-imido intermediate.[10e, 10f]

In addition to its relevance to reaction chemistry and high energy materials, tetrazene is of interest as a redox-non-innocent ligand. It is isobal to the common α-dimine ligand systems, and can, in principle, access at least three oxidation states, ranging from the neutral tetrazadiene to the dianionic tetrazenate (Figure 1):
Mössbauer spectroscopy. We report here the synthesis of the first manganese tetrazene complexes as the one-electron redox pair: \([\text{Mn}(\text{NR}_2)_2]_2\) and \([\text{Mn}(\text{NR}_2)_3]\), and discuss their electronic structures. In one crystalline morphology, evidence is seen for Mn(II) undergoing a reversible ring-opening reaction to give an imido/azide isomer detectable by X-ray crystallography and infrared spectroscopy. This behavior is absent in the second morphology.

**Results and Discussion**

![Scheme 1](image)

**Synthesis and Structures**

The Mn(III) and Mn(IV) complexes are synthesized from the Mn(II) precursor \([\text{Mn}[\text{NR}_2]_2]\) (R = Me₃Si) and adamantyl azide in the presence of \([\text{NH}_2\text{Bu}]\) ligands, which we have previously shown to favor oxidation of Mn(II). Since the strong \(σ\) and π-donation from amide and imide ligand system lowers the reduction potential of metals, favoring high oxidation states in mid-to-late transition metals. This approach was used to generate tris-hydrazide manganese(IV) propeller complexes previously by our group. Reaction of \([\text{Mn}[\text{NR}_2]_2]\) with AdN₃ in the presence of LiNH₂Bu gives a deep blue solution. Under these conditions, Mn(II) is oxidized and Mn(III) and Mn(IV) compounds are isolated. Mn(III) compounds are isolated as lithium salts, and presumably form by two-electron oxidation to Mn(IV) by azide followed by comproportionation with Mn(II) to give two equivalents of Mn(III). The reaction is thus mechanistically complex, and gives product mixtures, though the majority product tetrazene complexes are isolable in 12-35% yield following purification by extraction and crystallization.

Depending on the synthesis solvent, compound 1 may be isolated in two forms. When the compound is crystallized from tetrahydrofuran mother liquor, the 1-D polymer \([\text{Li}(\text{THF})_2\text{Mn}^{\text{III}}(\text{NR}_2)_2]_2\) (1-THF) is obtained. When the compound is crystallized from dimethoxyethane (DME) mother liquor, it is isolated as a DME-ligated adduct with product LiNR₂ and an unreacted equivalent of Mn[NR₂]₂. The resulting adduct takes the form of the ionic compound \([\text{Li(DME)}_2\text{Mn}^{\text{III}}(\text{NR}_2)_2]^+\text{[Mn}^{\text{II}}(\text{NR}_2)_3]^-\) (1-DME-LiMn[NR₂]₂).

The structure of 1-THF is that of a one-dimensional ionic polymer of \([\text{Mn}(\text{NR}_2)_2]\) units with intervening \([\text{Li}(\text{THF})_2]^+\) counterions (Fig. 2). The lithium atoms possess an up-down disorder placing each occupied lithium site proximal to one THF, and distal to the other. The structure of 1-DME-LiMn[NR₂]₂ is that of an ionic compound with a positive dillithium manganese tetrazene cation with the three-coordinate tris(bis(trimethylsilyl)amido)manganate(II) anion (Fig. 2). The oxidation state and charge of the \([\text{Mn}^{\text{III}}(\text{NR}_2)_3]\) anion is assigned by comparison of the Mn-N bond lengths (~2.05 Å) to literature, which matches well with Mn(II) but not with Mn(III). This assignment is further confirmed by UV-Visible absorption spectroscopy, which shows nearly identical spectral features (Fig. S2) for both 1-THF and 1-DME-LiMn[NR₂]₂, which are assigned to the \([\text{Mn}^{\text{III}}(\text{NR}_2)_3]\) unit, while the high-spin \([\text{Mn}^{\text{III}}(\text{NR}_2)_3]\) anion in 1-DME-LiMn[NR₂]₂ is colorless, having spin-forbidden electronic transitions, and contributes little to the spectrum.

When 1 is heated in acetonitrile, it reacts further, and extraction of the dried mixture into pentane gives the neutral adduct \([\text{Mn}(\text{NR}_2)_2]\) (2). This one-electron oxidized compound presumably forms via further disproportionation chemistry.

![Figure 2](image)
Converting the Mn(III)-containing 1 into 2, and a Mn(II)-based product which is left behind in the residue. In solution, 1 and 2 may be interconverted via a one-electron redox couple as indicated by the quasi-reversible cyclic voltammogram (Figure 3).

![Figure 3](image3.png)

Figure 3. Cyclic Voltammogram of 1-THF in MeCN solvent, showing quasi-reversible oxidation to 2 at -1.4 V vs. Fc.

Compound 2 crystalizes from pentane in pure form, giving a solid with a yellow-green appearance, or from acetonitrile as a solvent adduct (2-MeCN) as a purple-brown solid. Both structures exhibit molecular, pseudotetrahedral Mn(N4Ad)2 (2) as a neutral molecule, but while 2-MeCN is a highly ordered structure, pure 2 possesses significant disorder, attributed to a ring opening equilibrium of the metallacycle to give an azide-imido complex as a minor component (Figure 4). As illustrated in Figure 4, the disorder in the crystal structure of pure 2 is attributed to a ring opening equilibrium wherein the five-membered metallacycle converts to a terminal azide ligand and a terminal imido ligand. This behavior is reproducible in six crystal structures, all of which show a significant residual electron density peak ~ 1.1 Å away from the tetrazene ligand backbone (Figure S6), assigned as N(2B) and N(4B) (Fig. 4). Occupancies of the two disorder components with restraints upon the atomic thermal parameters refine to 93% of the ligand being in the tetrazene form, and 7% of the ligand being in the azide-imido form. Refinement without imposed restraints gives 96% and 4% for the components respectively, but with contracted thermal parameters on the γ-nitrogen atom. This is a dynamic disorder as evidenced by the temperature dependent occupancies of atoms N(2B) and N(4B) (Figure S7) suggesting an equilibrium interconversion between the two forms of the ligand set, which appears as a superposition of both ligand sets in the crystal structure. Therodynamic parameters for a single ring opening event are determined from van’t Hoff analysis (Figure S8) to be ΔH = 23.6(9) kJ/mol and ΔS = 0.018(5) kJ/mol/K.

It should be noted that while Figure 4 illustrates the ring-opened form of 2 as the bis(azide)bis(imido) structure as the crystallographic model, asymmetric single-ring-opened isomers are also expected to exist in equilibrium, with an approximate binomial distribution of the three species based upon the 93:7 crystalllographic occupancies:

![Scheme 2](image2.png)

Scheme 2. Statistical distribution of isomers of 2 in the solid state.

While the occupany of the opened form of the ligand is small (7%), the minor component can be assigned with good confidence for several reasons based on single-crystal X-ray data. First, least squares refinement of crystal structure parameters inherently provides experimental error (esd) for all parameters. In this case, the occupancy refinies with good confidence to 6.9 ± 0.4%, 7.7 ± 0.4%, and 9.4 ± 0.4% at -173, -95, and -33 °C respectively (Figure S8), indicating the electron density peak, though small, is well above the level of baseline noise. Second, the electron-density peak assigned to the ring-opened γ-nitrogen is reproducible, having been observed in the same positions in six out of six separate crystals of 2, while this peak is not observed in the well-ordered 2-MeCN morphology (Figure S7). Further, the N-N distances (1.12-1.14 Å) are consistent with azide, but fit poorly to other potential interatom assignments such as N-Li, (~2 Å expected), and the assignment of a proton ligated by N2-nitrogen atoms is unreasonable, having never been observed in any structure to our knowledge.

While evidence for ring opening equilibrium is found from single crystal X-ray data alone, further spectroscopic support was sought to check for consistency. The assignment of the disorder as a ring-opened azide-imido ligand set is supported by infrared spectroscopy (Figure 5), which shows several overlapping azide asymmetric stretches at around 2087 cm⁻¹ in freshly prepared samples of 2, but not in 2-MeCN. This observation is consistent with the presence of disorder in the crystal structure of 2 that does not exist in the structure of 2-MeCN. When 2 is synthesized using adamantyl azide...
isotopically labeled with $^{15}$N, the signature red-shifts by approximately 20 cm$^{-1}$, consistent with the expected vibrational isotope effect (Figure 5). The absence of N-H stretches in the 3200-3300 cm$^{-1}$ region supports the description of these ligands as imides as opposed to protonated amides.

This particular combination of azide and imido ligands on a metal is the most commonly proposed precursor to tetrazene. In previous work, this azide/imido ligand set has been shown to interconvert with tetrazene,$^{10b, 10d}$ but also, in another example, to represent kinetically trapped, separate products.$^{20}$ Assuming tetrazenes are synthesized from an azide/imido precursor ligand set, microscopic reversibility suggests that this ligand set may also represent a pathway for decomposition of tetrazenes.$^{10b, 10d}$

In this case, infrared spectroscopy reveals that the disordered structure of 2 decomposes at room temperature in air to give azide and an unidentified metal product, while the ordered structure of 2-MeCN does not undergo this decomposition on this timescale (figures S3, S4). The result suggests that the ring opening reaction may represent an activation pathway for tetrazene reactivity.

The NMR spectrum of 2 exhibits broad, paramagnetically shifted $^1$H NMR signatures whose relative intensities and positions vary with temperature. While this temperature-dependent behavior could be a result of the proposed equilibrium, we have not been successful in confidently assigning the NMR resonances. More likely, the observed shifts are a result in changes of magnetization of the paramagnetic manganese ion at different temperatures.

Density functional theory calculations discussed below support this isomerism. The optimized structure of the isolated, asymmetric single-ring-opened isomer of 2 is 114 kJ/mol higher in energy than the optimized tetrazene form. The doubly-opened bis(azide)/bis(imido) variant lies 242 kJ/mol higher than 2. The energy separation between the gas-phase isomers is considerably higher that estimated from variable temperature crystallography, primarily due to structural changes (such as expansion of the Mn-N bonds) that occur when the complex is considered apart from the solid state. However, the relative energy ordering is consistent with the trend seen in crystallographic occupancies.

Finally, the assignment of the disorder as ring-opened azide is consistent with a wealth of literature on the subject which has been reviewed$^{14}$ and has been previously supported experimentally$^{10b, 10d}$ though our work is the first crystallographic observation of the equilibrium phenomenon in the solid state.

**Electronic Structure**

Electronic structure assignments of redox non-innocent ligand complexes frequently invoke ligand bond metrics (Fig. 1) as a determining factor. However, this interpretation is not always straightforward, and metal-ligand bond polarization (e.g., $\pi$-bonding and $\pi$-backbonding) should be considered as an alternative electronic description of the phenomenon.$^{13a}$ In the case of 1, the electronic structure is fairly straightforward. The ligand bond metrics indicate longer N$_7$-N$_8$ bonds (1.33- 1.35 Å), and shorter N$_7$-N$_8$ (1.29-1.30 Å) bonds in both the structures of 1-THF and 1-DME:LiMn(NR$_2$)$_2$ (Table 1). Magnetic susceptibility measurements on 1-THF indicate a $\mu_{eff}$ of 5.09 Bohr magnetons, most consistent with the spin-only value of 4.90 Bohr magnetons for a high-spin $S = 2$ Mn(III) system. Thus, the standard assignment of 1 as a complex of Mn(III) with two dianionic tetrazene ligands is satisfied by all characterization data.

**Table 1.** Average experimental and theoretical metrics for Mn-N and N-N bonds in Mn-tetrazene complexes.

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>1-THF</th>
<th>1-DME</th>
<th>2</th>
<th>2-MeCN</th>
<th>2 (DFT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-N</td>
<td>1.976(8)</td>
<td>1.910(8)</td>
<td>1.924(4)</td>
<td>1.912(8)</td>
<td>2.010</td>
</tr>
<tr>
<td>N$_7$-N$_8$</td>
<td>1.341(11)</td>
<td>1.364(11)</td>
<td>1.341(5)</td>
<td>1.351(10)</td>
<td>1.322</td>
</tr>
<tr>
<td>N$_9$-N$_8$</td>
<td>1.295(17)</td>
<td>1.276(8)</td>
<td>1.303(8)</td>
<td>1.302(7)</td>
<td>1.301</td>
</tr>
</tbody>
</table>

[a] Metrics from X-ray structures are given as the average of all analogous but symmetrically inequivalent bonds with esd for the final digits shown in parenthesis.

In the case of 2, the two different crystal morphologies exhibit different bond length metrics in the tetrazene backbone. While the structure of 2-MeCN exhibits the normal long N$_7$-N$_8$ bonds and short N$_9$-N$_8$ bonds consistent with a Mn(IV) complex with dianionic tetrazene, the structure of 2 has intermediate bond lengths (as high as 1.31 for N$_7$-N$_8$ and 1.34 for N$_9$-N$_8$) for all N-N bonds, suggesting the possibility of ligand redox non-innocence, and that the electronic structure description of this compound might be better described as Mn(II) with two monoanionic tetrazyl radical ligands, analogous to a reported Ni$^{II}$([N$_7$Ar$_5$]$_2$) complex$^{11}$ or as a Mn(III) complex with a single radical anion ligand. Such valence tautomerism in manganese complexes has been a topic of interest, as formal transfer of an electron between the metal and redox-non-innocent ligand can lead to substantial reactivity differences.$^{21}$ Indeed, at first glance, it appears that a substantial difference in electronic structure between the two crystal morphologies is likely, as solid 2-MeCN crystals are dark purple-brown in appearance, while pure solid 2 crystals appear light yellow.
green. However, closer microscopic examination of crystals of 2 have revealed that these crystals are dichromatic, and are purple when back lit (transmission), but appear green when top lit due to the reflection of yellow-green light back to the observer (Figure 6). UV-Visible absorption spectroscopy of solutions of 2 vs. 2-MeCN are not informative as both solids dissolve to form an identical purple solution. Thus, if valence tautomerism exists, it does so only in the solid state.

EPR spectroscopy on solutions of 2 exhibit a rhombic $S = \frac{3}{2}$ signal with clear hyperfine coupling to a single manganese center observed in the $g_i$ signal (Fig. 7). This signal is consistent with a high spin Mn(IV) ion with three unpaired electrons. However, the alternative electronic structures of a high spin Mn(II) ion antiferromagnetically coupled to two ligand radical centers, or a high-spin Mn(III) ion antiferromagnetically coupled to a single ligand radical could also give rise to a similar $S = \frac{3}{2}$ signal. Thus, EPR alone is inconclusive.

To assign the oxidation state of Mn in pure crystals of 2, we turned to X-ray photoelectron spectroscopy in the 3s and 2p region. The observed binding energies in the $2p^{3/2}$ spectrum (Fig. 8) correspond better with high-spin Mn(IV) or Mn(III) than Mn(II), but fit best with Mn(III).[23] A match to Mn(II) is not supported as evidenced by the poor fit of the theoretical multiplet splittings, lack of a significant Auger satellite feature generally seen in high spin Mn(II) (Figure 8), and 3s splitting energy of 5.6 eV[24] (Figure S5). Thus, little evidence for a description of Mn(II) is observed from the XPS spectrum. Thus, the description of oxidation of each ligand by an electron to give Mn$^{3+}$(N$_2$Ar$_2$)$^-$ is consistent with XPS.

For comparison of electronic structure between solid and solution-phase 2, we obtained the EPR spectrum of solid 2, which shows a similar, but broadened signal to solution-phase 2, with an identical $g_z$ signal, but shifted $g_x$ and $g_y$ signatures. Combined with the XPS assignment of Mn(IV), the results suggest that the electronic structure of 2 is most likely analogous in both the solid state structures and in solution, and that redox tautomerism is not present.

Figure 6. Microscope images of a crystal of 2. 2 appears purple in transmission mode (back lit, left), but in reflection mode (top lit, right) and to the naked eye, green light is reflected back to the observer, making the crystal appear green (dichromism).

Figure 7. EPR spectra of 2 at 4 K, Mod Amplitude = 4.000G. Top: Spectrum in toluene solution. MW Freq: 9.643 GHz, MW Power: 0.201 mW, Middle: Simulation. Bottom: Spectrum of crystalline 2. MW Freq: 9.641 GHz, MW Power: 0.0201 mW. * marks a contaminant at $g = 2.273$ whose intensity varies among samples.

Figure 8. 2p$^{3/2}$ XPS spectrum (—) and fits of crystalline 2 to high spin Mn(IV) (—), Mn(III) (—), and Mn(II) (—).

The difference in bond metrics between 2 and 2-MeCN may be due to the presence of acetonitrile molecules in the structure of 2-MeCN, whose positively charged methyl ends are oriented near the tetrazene ligand backbone. This may serve to polarize Mn-N bonds, increasing electron density on the ligand HOMO. In contrast, in the absence of MeCN molecules, the ligands of 2 may be able to more strongly donate $\pi$-electron density into unoccupied metal-based orbitals. This possibility is supported by fitting of the XPS, which shows that the binding energies are shifted toward those expected for Mn(III) (Fig. 8). Another possibility is that the central metal may be Mn(III) with a single ligand radical either localized on one ligand, Mn$^{3+}$(N$_2$Ad)(N$_2$Ad$_2$)$_{-}$, and disordered within the crystal structure, or delocalized across both ligands. This description is most consistent with XPS, which fits Mn(III) extremely well. However, the Mn-N bonds in both 2 and 2-MeCN are quite short (~1.91 Å) based on X-ray crystallography, and more consistent with Mn(IV).[25] in contrast to the Mn-N bond lengths in 1 (~1.97 Å).
which are more consistent with Mn(III) \cite{26}. Finally, perturbations to the average atomic positions due to disorder in crystalline 2 could contribute to the observed differences in bond metrics between 2 and 2-MeCN.

For further consideration of the electronic structure of 2, we used density functional theory (DFT) calculations to examine the oxidation state of Mn and the ligand interactions. All calculations were performed using the B3LYP functional and a 6-311G** basis set for all atoms save Mn, which used a TZVP basis. This combination had previously been shown to give good results for delocalized σ-ligand complexes of 1st row transition metals.\cite{27} We examined two geometries: one with the Mn, N, and C atom positions taken from the crystal structure of 2-MeCN, and one with the geometry optimized by energy minimization. Geometry optimization gave comparable ligand N-N metrics to the crystal structure (Table 1), but the Mn-N bonds lengthened substantially from 1.91 to 2.01 Å. Despite the differences in Mn-N bond distances, the electronic structure calculated for the X-ray and optimized geometries was very similar. Examination of biorthogonalized wave functions of both structures reveals that the three unpaired electrons reside primarily on metal-based d-orbitals, nominally, dz^2, dx^2-y^2, and dxy, consistent with high-spin Mn(IV). However, Mulliken spin density summations count a total of ~4 \( \alpha \)-electrons on the metal and ~1 \( \beta \)-electron on the two tetrazene ligands (Figure 9).

Though an unpaired, ligand-based electron radical need not be invoked to describe the electronic structure, the DFT description is not inconsistent with redox non-innocence. The residence of four unpaired electrons on the metal is consistent with a formal Mn(III) ion, which is supported by X-ray photoelectron spectroscopy, which matches best to Mn(III). Nevertheless, XPS matches reasonably well with Mn(IV) as well, and the Mn-N bond lengths from X-ray crystallography are more consistent with Mn(IV) ligated by dianionic tetrazene ligands, and thus, this electronic structure description cannot be strictly ruled out. However, the description of the system as Mn(II) ion ligated by
two anion radical ligands is ruled out by both theory and experiment.

Conclusions

We have reported the synthesis of the first manganese tetrazene complexes as the redox pair 1 and 2, crystallized in a total of four morphologies. For 2, compound stability is highly dependent upon crystal morphology with pure crystals of 2 showing thermal instability and an equilibrium metallocycle ring opening reaction in the solid state while 2-MeCN lacks these features. Crystallographic and electronic structure characterization of 2 suggests that a Mn(II) ion with two anionic-radical tetrazene ligands is inconsistent with experiment. DFT calculations support an electronic structure described formally as a Mn(III) ion with a one-electron oxidized ligand set.

Experimental Section

General Methods

All manipulations were performed under a dry, anaerobic Ar atmosphere using Schlenk and glovebox techniques except where otherwise noted. Reagents and solvents were purchased from commercial vendors (Aldrich, Strem Chemicals), were of highest available purity, and were used without further purification unless otherwise noted. Anhydrous solvents such as pentane and acetonitrile were purified using an Innovative Technology, Inc. Pure Solv system and stored in the glovebox over activated 4 Å molecular sieves for at least 24 h before use. Tetrahydrofuran (THF), dimethoxyethane (DME), and hexamethyl disiloxane (HMDS) were distilled from sodium benzophenone ketyl under a nitrogen atmosphere and stored in the glovebox over 4 Å molecular sieves for 10 h. Mn(N(SiMe3))2Cl2[15] and N-labeled adamantyl azide were prepared according to published protocol.[26] Compounds 1 and 2 are air stable over short time periods and compound 2 was handled in air for FT-IR analysis. 1H NMR spectra were recorded on Bruker Avance 400 and 500 MHz spectrometers with spectral width of 200 ppm. Values for chemical shifts (ppm) are referenced to the residual protosolvent resonances. The magnetic susceptibility of 2 was measured by using an Alfa Aesar Magnetic Susceptibility balance, model mk1 c = 1.029. Elemental analyses were carried out under inert atmosphere by CENTE Element Analysis Facility, University of Rochester, Rochester, NY. Carbon values from elemental analysis generally were off. This phenomenon was previously observed and noted by Holland et al.[14] EPR spectroscopy was performed using a Bruker EMX X-band EPR spectrometer equipped with an Oxford Cryosystems liquid He cryostat. Infrared spectra were recorded in the range of 400-4000 cm⁻¹ on a Nicolet iS FTIR with an iD5 diamond ATR accessory. EPR data were simulated using the EasySpin software package for MATLAB.[24] Absorption spectra were recorded on a Shimadzu UV-2550 UV-Visible spectrophotometer. Density functional theory calculations were carried out using Gaussian 09 with the B3LYP functional, a Pople triple-zeta 6-311G* basis set for all atoms save Mn, and a TZVP basis for manganese. Calculations done at the experimental geometry used the 2-MeCN X-ray structure.

X-ray diffraction

Crystal diffraction data for all compounds were collected using a Bruker Kappa APEX II DUO diffractometer using Mo Kα radiation (λ = 0.71073) from a fine-focused sealed tube with a TRIUMPH monochromator. Data was collected at 100 K, and structures were solved using direct methods. The X-ray data of compound 1 and 2 was collected at 100 K by mounting of the crystal on a MTeGen loop using Apiezon-N grease. For VT studies, the crystal was mounted on a glass fiber with epoxy. Compounds in this support survived from low-intensity high angle data primarily due to disorder, which attenuates high-angle intensities due to destructive interference. All bond metrics are nevertheless considered in light of the associated experimental standard deviations of the bond length measurements.

The disordered ring-opened structure of 2 was discovered by the identification of a reproducible (in 6 structures) Fourier difference peak ~1.1 Å away from the tetrazene backbone. The height of this peak was typically 1.2-1.3 e⁻, greater than 10% of the height of the nearest atom (N, 7 e⁻) ruling out the possibility of a Fourier series truncation feature. The distance of this peak from the nitrogen atoms (1.1 Å) is too short for a N-Li contact (typically ~2 Å) and of the wrong geometry for a proton, which have never been observed to be bound in an n2 fashion to any nitrogen ligand to our knowledge.

Variable Temperature Crystallography

A single crystal of 2 was selected and mounted on a glass fiber using epoxy. The crystal was indexed to determine its orientation matrix, and a data collection strategy was developed. This crystal was then collected using this strategy three times at three different temperatures: 100K, 178K, and 240K. The structure was not collected at higher temperatures as 2 is seen to decompose at room temperature and above. The structure was solved using direct methods and refined using normal full-matrix least squares approaches (SHELXTL-2014/16). To determine occupancies of the azide ligands, thermal parameters on N(3) and N(6) (7 nitrogens of azide ligand) were tightly restrained, as these parameters correlate with occupancy parameters. With thermal parameters tightly restrained the occupancy k was refined freely using further refinement cycles to give temperature-dependent occupancies with good standard deviations.

Powder X-ray Diffraction

Powder patterns were collected from a sample of powdered mounted on a glass fiber in 180° scans about ϕ using Cu-Kα radiation from a sealed tube with a graphite monochromator. Powder patterns were simulated from single-crystal structures using Mercury 3.3 (CCDC).

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra (XPS) were collected with a Thermo Scientific K-alpha+ at the University of Delaware. XPS of the dry samples were collected using a monochromatic Al Kα X-rays (148.7 eV) generated from a rotating anode. Data were recorded using a high resolution, 300 mm mean radius hemispherical electrostatic analyzer. The base pressure of the analysis chamber was maintained at 1x10⁻⁹ Torr. Survey scans were collected using fixed pass energy of 300 eV and narrow scans were collected using a fixed pass energy of 150 eV. Data collected for the Mn 2p₃/₂ and Mn 3s spectral regions were peak fitted using Casa XPS software. To fit the Mn 2p₃/₂ region the procedure used by Nesbitt and Banerjee was employed.[21] The contributions of the Mn(IV) to the XPS data were fitted with peaks at 641.00, 642.07, 642.85, 643.88, and 644.99 eV using a relative peak area ratio of 1.0.0.60:0.31:0.09:0.05. Mn(III) contributions to the XPS data were fitted with peaks at 640.49,
641.19, 642.00, 643.02, and 644.39 eV with a relative peak area ratio of 0.860:0.861:0.056:0.17. Mn(II) contributions to the XPS data were fitted with peaks at 640.15, 641.65, 642.15, 643.05, and 644.55 eV using a relative peak area ratio of 1.0:0.710:0.480:0.30:0.30. Peak area ratios for each Mn-species were not changed during the fitting procedure. Peaks with a 50:50 Gaussian/Lorentzian contribution were used in the procedure and the full width half maximum for each peak was 1.5 eV. Using these parameters the spectral data was fitted by varying the relative contribution of individual set of multiplet peaks. Mn 3s peaks were identified at 89.9 and 84.3 eV, resulting in a splitting of 5.6 eV. and attributed to decomposition of 2 (possibly during the sample handling/mounting in air).

Mn(N$_2$Ad$_{10}$)$_3$·3 MeCN (2-MeCN). Compound 1 was dissolved in acetonitrile and stirred at room temperature for 4 hours in Ar atmosphere. 1 is only sparingly soluble in MeCN, and thus, the exact weight of dissolved 1 is not recorded. The resultant reaction mixture was filtered and kept at low temperature (−40°C) and brown-purple X-ray quality crystals are obtained in two days, which were filtered and dried.

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**References**


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Electronic structure of manganese complexes of the redox-non-innocent tetrazene ligand and evidence for the metal-azide/imido cycloaddition intermediate in formation and decomposition.