Polyazides

DOI: 10.1002/anie.201404735

Preparation of the First Manganese(III) and Manganese(IV) Azides[**]

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Abstract: *Fluoride-azide exchange reactions of Me_3SiN_3 with MnF_2 and MnF_3 in acetonitrile resulted in the isolation of $Mn(N_3)_2$ and $Mn(N_3)_3{\cdot}CH_3CN$, respectively. While $Mn(N_3)_2$ forms $[PPh_4]_2[Mn(N_3)_4]$ and $(bipy)_2Mn(N_3)_2$ upon reaction with PPh_4N_3 and 2,2′-bipyridine (bipy), respectively, the manganese(III) azide undergoes disproportionation and forms mixtures of $[PPh_4]_2[Mn(N_3)_4]$ and $[PPh_4]_2[Mn(N_3)_6]$, as well as $(bipy)_2Mn(N_3)_2$ and $(bipy)Mn(N_3)_4$. Neat and highly sensitive $Cs_2[Mn(N_3)_6]$ was obtained through the reaction of Cs_2MnF_6 with Me_3SiN_3 in CH_3CN.*

The synthesis of polyazido compounds has sparked much interest during the last two decades.[1] In general, polyazides are regarded as useful highly energetic materials owing to the endothermicity of the N_3 group. However, molecules containing a large number of azido groups are frequently explosive and shock sensitive. Not surprisingly, the synthesis and characterization of polyazido compounds can be regarded as one of the most challenging experimental tasks in synthetic chemistry.

Several azido compounds of manganese in the oxidation state +2 have been prepared and characterized. The first reported manganese azide is $Mn(N_3)_2$ which had been obtained by Wöhler et al. in 1917 by the reaction of $MnCO_3$ with HN_3.[2] However, the compound was only identified and characterized through elemental analysis and its heat of decomposition. The Vis[3] and IR spectra[4] were reported more than 50 years later. Salts containing the $[Mn(N_3)_4]^{2-}$ ion[3,5] have been prepared and the crystal structures of $[PPh_4]_2[Mn(N_3)_4]$[6] and $[MV][Mn(N_3)_4]$[7] (MV = methylviologen) have been determined. In addition, several manganese(II) coordination polymers with azido ligands have been reported and characterized structurally: $[MeNH_{4-x}][Mn(N_3)_3]$,[8] $Cs[Mn(N_3)_3]$,[9] $[NEt_4][Mn_2(N_3)_5(H_2O)]$,[9] $Mn(N_3)_2(L)(H_2O)_3$[10] (L = organic ligand), $Mn_4(L)_2(N_3)_8$,[11] $[Mn_2(L)_2(N_3)_2][Mn(N_3)_4(H_2O)_2]{\cdot}2\,H_2O$,[11] and $[Mn(L)(N_3)_2]_2[Mn(H_2O)_2(N_3)_2]$.[12] However, no manganese(III) or manganese(IV) azido compounds are known.

Herein, we report the preparation and characterization of $Mn(N_3)_3{\cdot}CH_3CN$, $[Mn(N_3)_6]^{2-}$, and $(bipy)Mn(N_3)_4$ (bipy = 2,2′-bipyridine) the first azido compounds of manganese in an oxidation state higher than +2. We also report the synthesis of the manganese(II) azides $Mn(N_3)_2$, $[Mn(N_3)_4]^{2-}$, and $(bipy)_2Mn(N_3)_2$, as well as the crystal structures of $[PPh_4]_2[Mn(N_3)_4]$, $[PPh_4]_2[Mn(N_3)_6]$, $(bipy)_2Mn(N_3)_2$, and $(bipy)Mn(N_3)_4$.

In analogy to our previously reported syntheses of inorganic polyazides,[13] manganese(II) fluoride was treated with an excess of trimethylsilyl azide in acetonitrile solution. This resulted in rapid and complete fluoride–azide exchange and the formation of a dark red solution [Eq. (1)].

$$MnF_2 + 2\,Me_3SiN_3 \xrightarrow[-2\,Me_3SiF]{CH_3CN} Mn(N_3)_2 \tag{1}$$

Removal of the volatile compounds (CH_3CN, Me_3SiF, and excess Me_3SiN_3) under vacuum at −20 °C results in the isolation of pure manganese diazide as a dark red to almost black solid. $Mn(N_3)_2$ is stable at ambient temperature but somewhat shock-sensitive. All attempts of growing single crystals suitable for an X-ray structure study were unsuccessful and the compound was characterized by its vibrational spectra (see Supporting Information). To further establish the identity of $Mn(N_3)_2$ and to examine its stabilization by anion or adduct formation, the diazide was treated with two equivalents of PPh_4N_3 and bipy, respectively, in acetonitrile solution. With PPh_4N_3, the corresponding tetrazido manganate(II) $[PPh_4]_2[Mn(N_3)_4]$ was obtained and the reaction with 2,2′-bipy led to the isolation of the 2:1 donor adduct $(bipy)_2Mn(N_3)_2$. $[PPh_4]_2[Mn(N_3)_4]$ and $(bipy)_2Mn(N_3)_2$ can also be obtained in a more convenient, single-step route through the reaction of MnF_2 with Me_3SiN_3 in the presence of two equivalents of PPh_4N_3 or bipy, respectively, in acetonitrile solution [Eq. (2) and (3)].

$$MnF_2 + 2\,Me_3SiN_3 + 2\,PPh_4N_3 \xrightarrow[-2\,Me_3SiF]{CH_3CN} [PPh_4]_2[Mn(N_3)_4] \tag{2}$$

$$MnF_2 + 2\,Me_3SiN_3 + 2\,bipy \xrightarrow[-2\,Me_3SiF]{CH_3CN} (bipy)_2Mn(N_3)_2 \tag{3}$$

$[PPh_4]_2[Mn(N_3)_4]$ and $(bipy)_2Mn(N_3)_2$ were obtained as beige/brown and orange, respectively, and insensitive crystalline solids. They were characterized by their vibrational spectra and X-ray crystal structures,[14] as well as their decomposition temperatures, impact and friction sensitivities

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[**] This work was funded by the Office of Naval Research (ONR), the Air Force Office of Scientific Research (AFOSR), and the Defense Threat Reduction Agency (DTRA). We appreciate NSF CRIF grant 1048807 for the support of an X-ray diffractometer. We thank Profs. G. K. S. Prakash and G. A. Olah for their steady support, and Drs. M. Rahm, W. Wilson, and R. Wagner as well as G. B.-Chabot, P. Deokar, and A. Baxter for their help and stimulating discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201404735.

(see Supporting Information).

The reaction of manganese(III) fluoride with trimethylsilyl azide in acetonitrile solution resulted again, in the formation of a dark red solution. Removal of the volatile compounds (CH_3CN, Me_3SiF, and excess Me_3SiN_3) under vacuum at ambient temperature resulted in the isolation of the corresponding manganese triazide acetonitrile adduct as a dark red to almost black solid [Eq. (4)].

$$MnF_3 + 3\,Me_3SiN_3 \xrightarrow[-3\,Me_3SiF]{CH_3CN} Mn(N_3)_3 \cdot CH_3CN \tag{4}$$

$Mn(N_3)_3{\cdot}CH_3CN$ is stable at ambient temperature but shock-sensitive and explodes upon heating. It was not possible to remove the coordinated acetonitrile molecule under vacuum at slightly elevated temperatures (40°C). Attempts of growing single crystals of $Mn(N_3)_3{\cdot}CH_3CN$ were unsuccessful and the compound was identified and characterized by its vibrational spectra and the observed material balance (see Supporting Information).

When $Mn(N_3)_3{\cdot}CH_3CN$ was treated with two equivalents of PPh_4N_3 in acetonitrile solution, the manganese(III) compound disproportionated into manganese(II) and manganese(IV) giving a mixture of $[PPh_4]_2[Mn(N_3)_4]$ and $[PPh_4]_2[Mn(N_3)_6]$. Such a mixture of $[PPh_4]_2[Mn(N_3)_4]$ and $[PPh_4]_2[Mn(N_3)_6]$ could be obtained directly by the reaction of MnF_3 with Me_3SiN_3 and two equivalents of PPh_4N_3 in acetonitrile [Eq. (5)].

$$2\,MnF_3 + 6\,Me_3SiN_3 + 4\,PPh_4N_3 \xrightarrow[-6\,Me_3SiF]{CH_3CN} [PPh_4]_2[Mn(N_3)_4] + [PPh_4]_2[Mn(N_3)_6] \tag{5}$$

$[PPh_4]_2[Mn(N_3)_4]$ and $[PPh_4]_2[Mn(N_3)_6]$ were isolated as an insensitive mixture of dark red (Mn^{II}) and orange (Mn^{IV}) crystals. Both azidomanganate salts were identified and characterized by their vibrational spectra and X-ray crystal structures[14] (see Supporting Information). No attempts were made to separate the two compounds other than sorting out the crystals under a microscope. It was also not attempted to quantify the exact ratio of the two compounds. However, based on visual inspection of reaction mixtures under a microscope and their intensity pattern in the IR and Raman spectra, the compounds appear to be formed in an equimolar ratio.

A neat hexaazidomanganate(IV) salt was obtained as a dark red precipitate in the reaction of Cs_2MnF_6 with Me_3SiN_3 in acetonitrile at −20°C [Eq. (6)]. The compound was isolated after removal of all volatile materials under vacuum at −20°C.

$$Cs_2MnF_6 + 6\,Me_3SiN_3 \xrightarrow[-6\,Me_3SiF]{CH_3CN} Cs_2[Mn(N_3)_6] \tag{6}$$

While the mixtures of $[PPh_4]_2[Mn(N_3)_4]$ and $[PPh_4]_2[Mn(N_3)_6]$ are very stable solids that can be handled at ambient temperature, $Cs_2Mn(N_3)_6$ is a very sensitive and treacherous compound that should be handled with extreme caution. On one occasion, a sample of pure $Cs_2[Mn(N_3)_6]$ at −78°C exploded violently without external provocation. Therefore, this compound was characterized only by its low-temperature Raman spectrum (see Supporting Information).

The reaction of $Mn(N_3)_3{\cdot}CH_3CN$ with bipy in acetonitrile solution resulted again in a disproportionation of the manganese(III) azide into manganese(II) and manganese(IV) compounds, giving a mixture of $(bipy)_2Mn(N_3)_2$ and $(bipy)Mn(N_3)_4$. Similarly, a mixture of $(bipy)_2Mn(N_3)_2$ and $(bipy)Mn(N_3)_4$ was obtained by the one-step reaction of MnF_3 with Me_3SiN_3 in the presence of 1.5 equivalents of bipy in acetonitrile [Eq. (7)].

$$2\,MnF_3 + 6\,Me_3SiN_3 + 3\,bipy \xrightarrow[-6\,Me_3SiF]{CH_3CN} (bipy)_2Mn(N_3)_2 + (bipy)Mn(N_3)_4 \tag{7}$$

The compounds $(bipy)_2Mn(N_3)_2$ and $(bipy)Mn(N_3)_4$ were obtained as a mixture of dark red (Mn^{II}) and orange (Mn^{IV}) crystals. Both manganese(IV) azide adducts were identified and characterized by their vibrational spectra and X-ray crystal structures[14] (see Supporting Information). No attempts were made to separate both compounds other than sorting out a few crystals under a microscope. It was also not attempted to quantify the exact ratio of the two compounds. However, based on visual inspection of reaction mixtures under a microscope and their intensity pattern in the IR and Raman spectra, the compounds appear to be formed in an equimolar ratio.

The crystal structure of $(bipy)_2Mn(N_3)_2$ (Figure 1 and Supporting Information) contains isolated and well separated molecules.[14] The closest intermolecular N–N and M–N distances involving azido groups are 4.699(3) Å and 5.588(3) Å, respectively. The structure consists of an asymmetric $(bipy)MnN_3$ unit. The second azido and bipy ligands are generated by symmetry. The observed average $Mn{-}N_{azido}$ distance of 2.167(1) Å lies between those reported for $[Mn(N_3)_4]^{2-}$ (2.04(5) Å) in $[PPh_4]_2[Mn(N_3)_4]$[6] and $[Mn(N_3)_3]^-$ in $[NMe_4][Mn(N_3)_3]$ (2.23(2) Å).[8a] The N–N distances in the azido ligands are found to 1.1922(13) Å and 1.1644(13) Å.

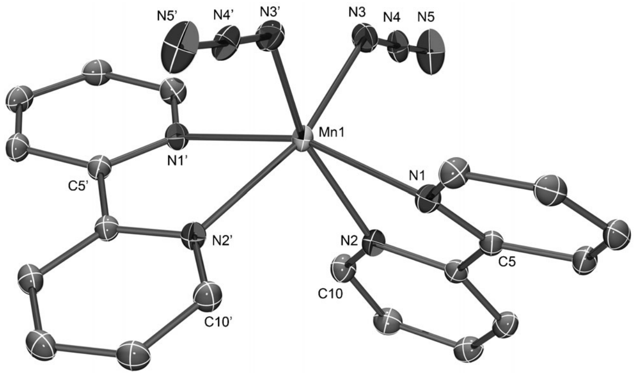

Figure 1. Crystal structure of $(bipy)_2Mn(N_3)_2$. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Mn1–N1 2.3234(8), Mn1–N2 2.2655(9), Mn1–N3 2.1673(9), N3–N4 1.1922(13), N4–N5 1.1644(13); N1-Mn1-N1′ 159.34(4), N1-Mn1-N2′ 94.68(3), N3-Mn1-N3′ 91.91(5).

$(bipy)Mn(N_3)_4$ crystallizes in the monoclinic space group *C*2/*c*.[14] The structure consists of isolated molecules with a distorted pseudo-octahedral environment around the central manganese atom (Figure 2). The closest intermolecular N–N and Mn–N distances involving azido ligands are 3.103(3) Å and 4.663(3) Å, respectively. The structure consists of an asymmetric $(C_5H_4)NMn(N_3)_2$ unit with two azido groups and half of a bipy ligand covalently bonded in a trigonal pyramidal fashion to the manganese. The remaining azido groups and the missing half of the bipy ligand are generated through symmetry. The average $Mn–N_{azido}$ distance is found to 1.940(2) Å and the average N–N distances in the azido ligands are 1.218(2) and 1.142(2) Å.

Our crystal structure[14] of $[PPh_4]_2[Mn(N_3)_4]$ is in good agreement with the one reported previously.[6] Similarly to the previous structure, our structure suffers from a positional disorder of the azido ligands, resulting in large uncertainties in bond lengths and angles for the tetraazido anion. Further details and figures for $[PPh_4]_2[Mn(N_3)_4]$ are given in the Supporting Information.

$[PPh_4]_2[Mn(N_3)_6]$ crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in the unit cell.[14] The structure consists of isolated and well-separated $[PPh_4]^+$ and $[Mn(N_3)_6]^{2-}$ ions. The closest intermolecular N–N and Mn–N distances are 4.996(3) and 7.316(2) Å, respectively. Figure 3 depicts the structure of the $[Mn(N_3)_6]^{2-}$ ion that is only slightly distorted from perfect S_6 symmetry. The observed structure of the $[Mn(N_3)_6]^{2-}$ ion is in good agreement with the propeller-type S_6 structure predicted by theoretical calculations and the ones previously found for the similar hexaazides $[In(N_3)_6]^{3-}$,[15] $[Tl(N_3)_6]^{3-}$,[15] $[Si(N_3)_6]^{2-}$,[16] $[Ge(N_3)_6]^{2-}$,[17] $[As(N_3)_6]^{-}$,[18] $[Sb(N_3)_6]^{-}$,[19] $[Se(N_3)_6]^{2-}$,[20] $[Ti(N_3)_6]^{2-}$,[21] $[V(N_3)_6]^{2-}$,[22] $[Nb(N_3)_6]^{-}$,[23] $[Ta(N_3)_6]^{-}$,[23] and $W(N_3)_6$,[24] but contrary to that of $[Te(N_3)_6]^{2-}$ [25] and $[Bi(N_3)_6]^{3-}$ [26] for which the free valence electron pair at the central atom becomes sterically active. The structure consists of an asymmetric MnN_9 unit with three azido groups covalently bonded in a trigonal pyramidal fashion to the manganese. The remaining three azide groups are generated by symmetry (symmetry operation $-x,1-y,1-z$). The observed average Mn–N distance of 1.991(2) Å lies between the one observed for $(bipy)Mn(N_3)_4$ (1.940(2) Å) and the ones found for $(bipy)_2Mn(N_3)_2$ (2.167(1) Å) and $[Mn(N_3)_4]^{2-}$ (2.05(2) Å).

The vibrational spectra of $Mn(N_3)_3{\cdot}CH_3CN$ and $Cs_2[Mn(N_3)_6]$ are depicted in Figures 4 and 5, respectively. The infrared spectra of the manganese azides are primarily dominated by the bands assigned to the $\nu_{as}(N_3)$ vibration modes in the region 1900–2100 cm^{-1}. As expected for covalent azides, the Raman spectra of the manganese azides exhibit the signals of the $\nu_{as}(N_3)$ vibration modes in the region 1900–2100 cm^{-1}. The Mn-N_3 vibration modes are found in the 350–400 cm^{-1} region. These two modes account for the strongest bands in the Raman spectra of $Mn(N_3)_2$, $Mn(N_3)_3{\cdot}CH_3CN$, and $Cs_2[Mn(N_3)_6]$, while the spectra of $(bipy)_2Mn(N_3)_2$, $(bipy)Mn(N_3)_4$, $[PPh_4]_2[Mn(N_3)_4]$, and $[PPh_4]_2[Mn(N_3)_6]$ are dominated by bands of the organic moieties. A characteristic feature for the presence of coordinated CH_3CN in $Mn(N_3)_3{\cdot}CH_3CN$ is the presence of the two bands of almost equal intensity at 2318 and 2291 cm^{-1} in the vibrational spectra which can be attributed to the $\nu(CN)$ vibration. Such splitting of the $\nu(CN)$ vibration in coordinated CH_3CN has been observed previously.[23]

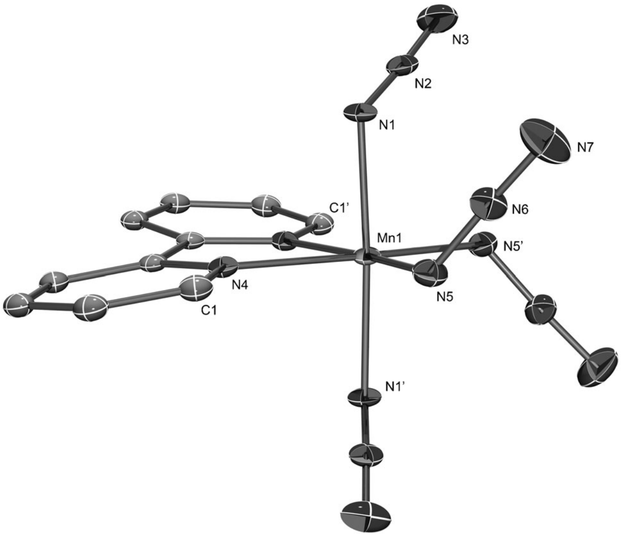

Figure 2. Crystal structure of $(bipy)Mn(N_3)_4$. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Mn1–N1 1.9623(13), Mn1–N4 2.0720(13), Mn1–N5 1.9178(14), N1–N2 1.214(2), N2–N3 1.145(2), N5–N6 1.222(2), N6–N7 1.139(2); N1-Mn1-N1′ 176.54(8), N1-Mn1-N5 91.71(6), N1-Mn1-N5′ 90.59(6).

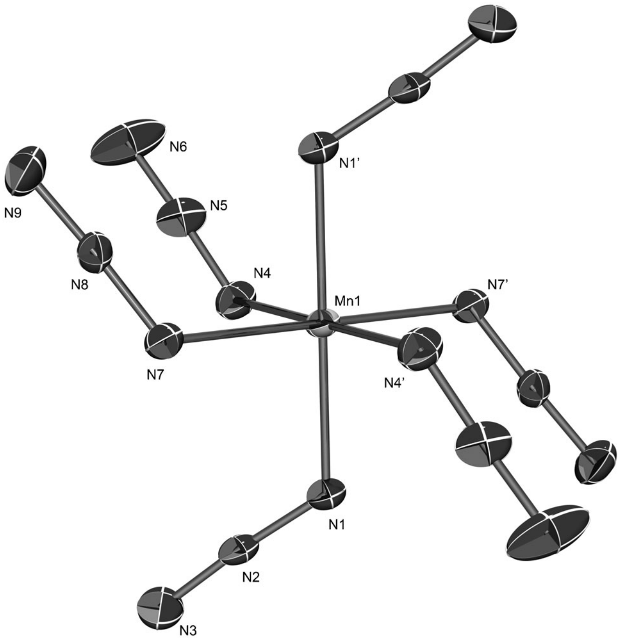

Figure 3. The anion in the crystal structure of $[PPh_4]_2[Mn(N_3)_6]$. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Mn1–N1 1.9716(11), Mn1–N4 2.0087(12), Mn1–N7 1.9936(11), N1–N2 1.205(2), N2–N3 1.147(2), N4–N5 1.206(2), N5–N6 1.147(2), N7–N8 1.212(2), N8–N9 1.143(2); N1-Mn1-N1′ 180.00(3), N1-Mn1-N4 90.12(5), N1-Mn1-N7 90.53(5).

The stabilities of the manganese polyazido compounds were determined using differential thermal analysis (DTA) scans, BAM impact and friction sensitivity testers and are summarized in Table 1. Among the polyazido compounds of this study, only $Mn(N_3)_3{\cdot}CH_3CN$ exploded upon heating

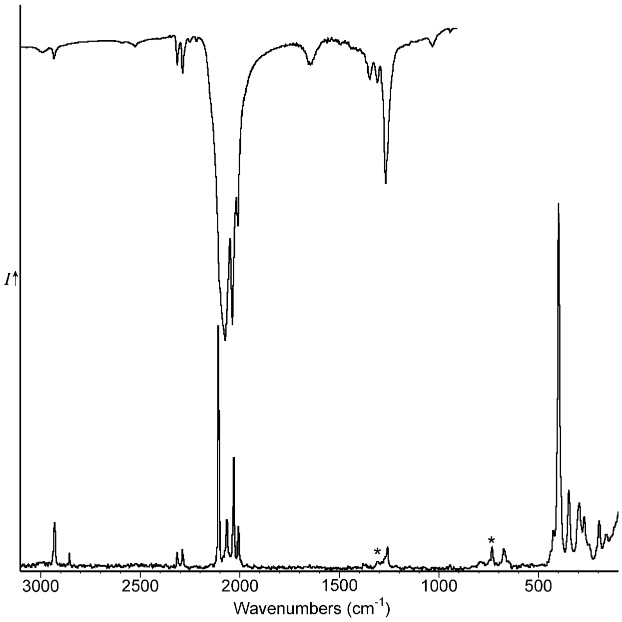

Figure 4. The IR spectrum (upper trace) and low-temperature Raman spectrum (lower trace) of $Mn(N_3)_3 \cdot CH_3CN$. Bands marked by asterisks (*) are due to the FEP sample container.

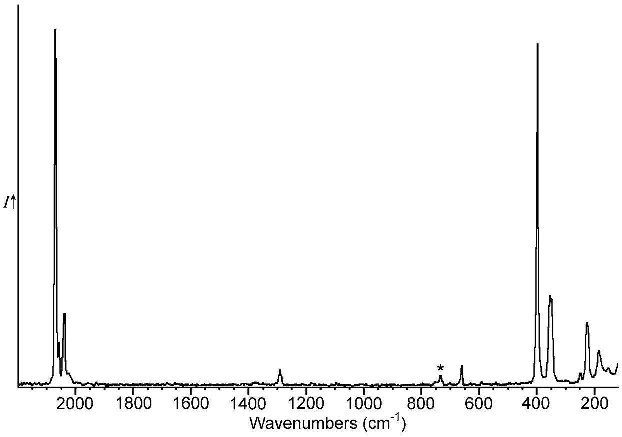

Figure 5. The low-temperature Raman spectrum of $Cs_2[Mn(N_3)_6]$. The band marked by an asterisk (*) is due to the FEP sample container.

Table 1: Stabilities of the manganese polyazides.[a]

Compound	T_d [°C][a]	IS [J][a]	FS [N][a]
$Mn(N_3)_2$	296	>100	>240
$(bipy)_2Mn(N_3)_2$	260[b]	>100	>240
$[PPh_4]_2[Mn(N_3)_4]$	247	>100	>240
$Mn(N_3)_3 \cdot CH_3CN$	102[c]	2	<5
$(bipy)_2Mn(N_3)_2$/$(bipy)Mn(N_3)_4$ mixture	261[b] 307	3	<5
$[PPh_4]_2[Mn(N_3)_4]$/$[PPh_4]_2[Mn(N_3)_6]$ mixture	250	80	>240

[a] T_d decomposition temperature, IS impact sensitivity, FS friction sensitivity. [b] Endothermic. [c] Explosion.

(102 °C explosion temperature). The remaining compounds showed smooth decomposition upon heating at a rate of 5 °C min^{-1}. With the exception of $Mn(N_3)_3 \cdot CH_3CN$, all the investigated manganese azides show high thermal stabilities with determined decomposition temperatures of more than 240 °C. The tetraazido manganese(II) salt $[PPh_4]_2[Mn(N_3)_4]$ melts at 160 °C and decomposes exothermic upon further heating at 247 °C. For the 2,2′-bipyridine adduct $(bipy)_2Mn(N_3)_2$, no exothermic decomposition could be determined. The DTA scan up to 400 °C shows a melting point of about 65 °C and an endothermic decomposition at about 260 °C. The mixture of $(bipy)_2Mn(N_3)_2$ and $(bipy)Mn(N_3)_4$ shows two endothermic peaks at about 65 °C and 261 °C and an exothermic decomposition at 307 °C. The mixture of $[PPh_4]_2[Mn(N_3)_4]$ and $[PPh_4]_2[Mn(N_3)_6]$ mixture decomposes at 250 °C.

The determined impact and friction sensitivities reveal a similar pattern. The manganese(II) azides appear to be insensitive with impact and friction sensitivities of more than 100 J and 240 N, respectively. $[PPh_4]_2[Mn(N_3)_6]$ is somewhat sensitive as can be seen by the moderate impact sensitivity of the $[PPh_4]_2[Mn(N_3)_4]$ and $[PPh_4]_2[Mn(N_3)_6]$ mixture. $Mn(N_3)_3 \cdot CH_3CN$ and $(bipy)Mn(N_3)_4$ are highly sensitive and can be classified as primary explosives.

In summary, the first manganese(III) and manganese(IV) azides have been prepared and characterized. The binary manganese azides $Mn(N_3)_2$ and $Mn(N_3)_3 \cdot CH_3CN$ have been obtained from the corresponding manganese fluorides by fluoride–azide exchange with Me_3SiN_3 in CH_3CN solution. Both azides show a distinguished difference in their reaction behavior. The reactions of $Mn(N_3)_2$ with 2,2-bipyridine and PPh_4N_3 lead to the formation of the manganese(II) products $(bipy)_2Mn(N_3)_2$ and $[PPh_4]_2[Mn(N_3)_4]$, respectively. In contrast, the reactions of 2,2-bipyridine and PPh_4N_3 with the manganese(III) azide resulted in disproportionations into manganese(II) and manganese(IV) under formation of equimolar mixtures of $(bipy)_2Mn(N_3)_2$ and $(bipy)Mn(N_3)_4$, and $[PPh_4]_2[Mn(N_3)_4]$ and $[PPh_4]_2[Mn(N_3)_6]$, respectively. The fluoride–azide exchange reaction between Cs_2MnF_6 and Me_3SiN_3 resulted in the formation and isolation of very sensitive and highly explosive $Cs_2[Mn(N_3)_6]$. All manganese azides were characterized by their vibrational spectra and, in the case of $(bipy)_2Mn(N_3)_2$, $(bipy)Mn(N_3)_4$, $[PPh_4]_2[Mn(N_3)_4]$, and $[PPh_4]_2[Mn(N_3)_6]$, by their X-ray crystal structures.

Experimental Section

Caution! Polyazides are extremely shock-sensitive and can explode violently upon the slightest provocation. Because of the high energy content and high detonation velocities of these azides, their explosions are particularly violent and can cause, even on a one mmol scale, significant damage. Neat $Cs_2[Mn(N_3)_6]$ is a very treacherous and highly explosive compound. A sample of the compound exploded without external provocation at −78 °C. The use of appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing, such as heavy leather welding suits and ear plugs)[27] is mandatory. **Ignoring safety precautions can lead to serious injuries!**

Materials and Apparatus: All reactions were carried out in Teflon-FEP ampules that were closed by stainless steel valves. Volatile materials were handled in a Pyrex glass vacuum line. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. The starting materials MnF_2, MnF_3 (both Strem), and 2,2′-bipyridine (bipy) (Aldrich) were used without further purification. Trimethylsilyl azide (Aldrich) was purified by fractional condensation. PPh_4N_3[28] and Cs_2MnF_6[29] were prepared according to literature procedures. Solvents were dried by standard methods and freshly distilled prior to use.

Crystal structure determinations: The single crystal X-ray diffraction data were collected on a Bruker SMART APEX DUO diffractometer with the χ-axis fixed at 54.74° and using Mo K_α radiation (TRIUMPH curved-crystal monochromator) from a fine-focus tube. The diffractometer was equipped with an APEX II CCD detector and an Oxford Cryosystems Cryostream 700 apparatus for low-temperature data collection. A complete hemisphere of data was scanned on omega and phi (0.5°) at a detector resolution of 512 × 512. The frames were then integrated using the SAINT algorithm to give the *hkl* files corrected for Lp/decay.[30] The absorption correction was performed using the SADABS program.[31] The structures were solved by the direct method and refined on F^2 using the Bruker SHELXTL Software Package.[32] All non-hydrogen atoms were refined anisotropically. ORTEP drawings were prepared using the ORTEP-3 for Windows V2.02 program.[33]

$Mn(N_3)_2$ and $Mn(N_3)_3\cdot CH_3CN$: A sample of MnF_2 (155 mg; 1.67 mmol) or MnF_3 (112 mg; 1.00 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of CH_3CN (2.0 mL) and Me_3SiN_3 (4.00 mmol) in vacuo at −196 °C. The mixture was allowed to warm to ambient temperature. After 10 h, all volatile material was removed under vacuum at −20 °C leaving behind dark colored solids.

$(bipy)_2Mn(N_3)_2$: A sample of MnF_2 (139 mg; 1.50 mmol) and 2,2′-bipy (469 mg; 3.00 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of CH_3CN (1.5 mL) and Me_3SiN_3 (460 mg, 4.00 mmol) in vacuo at −196 °C. The mixture was allowed to warm to ambient temperature. After 10 h, an orange-red solution with a small amount of beige precipitate was obtained. The supernatant solution was transferred into another Teflon-FEP ampule and all volatile material was removed under vacuum at −20 °C, leaving behind orange crystals.

$[PPh_4]_2[Mn(N_3)_4]$: A sample of MnF_2 (93 mg; 1.00 mmol) and PPh_4N_3 (763 mg; 2.00 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of CH_3CN (2.0 mL) and Me_3SiN_3 (345 mg, 3.00 mmol) in vacuo at −196 °C. The mixture was allowed to warm to ambient temperature. After 10 h, a dark solution with a small amount of beige precipitate was obtained. The supernatant solution was transferred into another Teflon-FEP ampule and all volatile material removed under vacuum at −20 °C, leaving behind beige to brown crystals.

Reaction of MnF_3 with Me_3SiN_3 and 2,2′-bipy: A sample of MnF_3 (112 mg; 1.00 mmol) and 2,2′-bipy (235 mg; 1.5 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of CH_3CN (2.0 mL) and Me_3SiN_3 (461 mg, 4.00 mmol) in vacuo at −196 °C. The mixture was allowed to warm to ambient temperature. After 10 h, a red solution was obtained. All volatile material was removed under vacuum at −20 °C, leaving behind a mixture of orange-red and dark-red crystals.

Reaction of MnF_3 with Me_3SiN_3 and PPh_4N_3: A sample of MnF_3 (112 mg; 1.00 mmol) and PPh_4N_3 (763 mg; 2.00 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of CH_3CN (2.0 mL) and Me_3SiN_3 (461 mg, 4.00 mmol) in vacuo at −196 °C. The mixture was allowed to warm to ambient temperature. After 10 h, a red solution was obtained. All volatile material was removed under vacuum at −20 °C, leaving behind a mixture of orange and dark-red crystals.

Preparation of $Cs_2[Mn(N_3)_6]$: A sample of Cs_2MnF_6 (100 mg; 0.23 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of CH_3CN (1.0 mL) and Me_3SiN_3 (461 mg, 4.00 mmol) in vacuo at −196 °C. The mixture was allowed to warm to ambient temperature and occasionally agitated. After 10 h, the color of the precipitate had changed from initially yellow to dark red. The mixture was cooled to −78 °C and a Raman spectrum of the precipitate obtained. The mixture was then warmed to −20 °C and all volatile material removed under vacuum, leaving behind a dark red solid.

Further experimental details can be found in the Supporting Information.

Received: April 27, 2014

Keywords: azides · disproportionation · manganese · polyazides · structure elucidation

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[1] W. P. Fehlhammer, W. Beck, *Z. Anorg. Allg. Chem.* **2013**, *639*, 1053 – 1082.
[2] L. Wöhler, F. Martin, *Ber. Dtsch. Chem. Ges.* **1917**, *50*, 586 – 596.
[3] V. Gutmann, W. Lux, *J. Inorg. Nucl. Chem.* **1967**, *29*, 2391 – 2399.
[4] K. Dehnicke, R. Dübgen, *Z. Anorg. Allg. Chem.* **1978**, *444*, 61 – 70.
[5] a) W. Beck, W. P. Fehlhammer, P. Pöllmann, E. Schuierer, K. Feldl, *Chem. Ber.* **1967**, *100*, 2335 – 2361; b) W. Beck, K. Feldl, E. Schuierer, *Angew. Chem.* **1965**, *77*, 458 – 459.
[6] K. Steiner, W. Willing, U. Müller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1987**, *555*, 7 – 15.
[7] Y. Ma, A.-L. Cheng, W.-W. Sun, J.-Y. Zhang, E.-Q. Gao, *Inorg. Chem. Commun.* **2009**, *12*, 412 – 416.
[8] a) F. A. Mautner, R. Cortes, L. Lezama, T. Rojo, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 78 – 80; *Angew. Chem.* **1996**, *108*, 96 – 98; b) F. A. Mautner, S. Hanna, R. Cortes, L. Lezama, M. G. Barandika, T. Rojo, *Inorg. Chem.* **1999**, *38*, 4647 – 4652; c) X.-H. Zhao, X.-C. Huang, S.-L. Zhang, D. Shao, H.-Y. Wei, X.-Y. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 16006 – 16009.
[9] M. A. S. Goher, J. Cano, Y. Journaux, M. A. M. Abu-Youssef, F. A. Mautner, A. Escuer, R. Vicente, *Chem. Eur. J.* **2000**, *6*, 778 – 784.
[10] a) Q. Liu, X. Q. Sung, J. Z. Zou, Z. Xu, K. B. Yu, *J. Coord. Chem.* **2002**, *55*, 1021 – 1027; b) B. Bitschnau, A. Egger, A. Escuer, F. A. Mautner, B. Sodin, R. Vicente, *Inorg. Chem.* **2006**, *45*, 868 – 876; c) H.-L. Sun, Z.-M. Wang, S. Gao, *Chem. Eur. J.* **2009**, *15*, 1757 – 1764.
[11] Y.-Q. Wang, Q.-X. Jia, K. Wang, A.-L. Cheng, E.-Q. Gao, *Inorg. Chem.* **2010**, *49*, 1551 – 1560.
[12] B. Shaabani, A. A. Khandar, M. Dusek, M. Pojarova, F. Mahmoudi, A. Feher, M. Kajnakova, *J. Coord. Chem.* **2013**, *66*, 748 – 762.
[13] R. Haiges, A. Vij, J. A. Boatz, S. Schneider, T. Schroer, M. Gerken, K. O. Christe, *Chem. Eur. J.* **2004**, *10*, 508 – 517.
[14] CCDC 995666, 995667, 995668, 995669 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[15] R. Haiges, J. A. Boatz, J. M. Williams, K. O. Christe, *Angew. Chem. Int. Ed.* **2011**, *50*, 8828 – 8833; *Angew. Chem.* **2011**, *123*, 8990 – 8995.
[16] A. C. Filippou, P. Portius, G. Schnakenburg, *J. Am. Chem. Soc.* **2002**, *124*, 12396 – 12397.
[17] A. C. Filippou, P. Portius, D. U. Neumann, K. D. Wehrstedt, *Angew. Chem. Int. Ed.* **2000**, *39*, 4333 – 4336; *Angew. Chem.* **2000**, *112*, 4524 – 4527.
[18] a) K. Karaghiosoff, T. M. Klapötke, B. Krumm, H. Nöth, T. Schutt, M. Suter, *Inorg. Chem.* **2002**, *41*, 170 – 179; b) T. M. Klapötke, H. Nöth, T. Schütt, M. Warchhold, *Angew. Chem. Int. Ed.* **2000**, *39*, 2108 – 2109; *Angew. Chem.* **2000**, *112*, 2197 – 2199.
[19] R. Haiges, J. A. Boatz, A. Vij, V. Vij, M. Gerken, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem. Int. Ed.* **2004**, *43*, 6676 – 6680; *Angew. Chem.* **2004**, *116*, 6844 – 6848.

[20] T. M. Klapötke, B. Krumm, M. Scherr, R. Haiges, K. O. Christe, *Angew. Chem. Int. Ed.* **2007**, *46*, 8686 – 8690; *Angew. Chem.* **2007**, *119*, 8840 – 8845.

[21] R. Haiges, J. A. Boatz, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem. Int. Ed.* **2004**, *43*, 3148 – 3152; *Angew. Chem.* **2004**, *116*, 3210 – 3214.

[22] R. Haiges, J. A. Boatz, K. O. Christe, *Angew. Chem. Int. Ed.* **2010**, *49*, 8008 – 8012; *Angew. Chem.* **2010**, *122*, 8180 – 8184.

[23] R. Haiges, J. A. Boatz, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem. Int. Ed.* **2006**, *45*, 4830 – 4835; *Angew. Chem.* **2006**, *118*, 4948 – 4953.

[24] R. Haiges, J. A. Boatz, R. Bau, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem. Int. Ed.* **2005**, *44*, 1860 – 1865; *Angew. Chem.* **2005**, *117*, 1894 – 1899.

[25] R. Haiges, J. A. Boatz, A. Vij, M. Gerken, S. Schneider, T. Schroer, K. O. Christe, *Angew. Chem. Int. Ed.* **2003**, *42*, 5847 – 5851; *Angew. Chem.* **2003**, *115*, 6027 – 6031.

[26] a) R. Haiges, M. Rahm, D. A. Dixon, E. B. Garner, K. O. Christe, *Inorg. Chem.* **2012**, *51*, 1127 – 1141; b) K. Rosenstengel, A. Schulz, A. Villinger, *Inorg. Chem.* **2013**, *52*, 6110 – 6126; c) A. Villinger, A. Schulz, *Angew. Chem. Int. Ed.* **2010**, *49*, 8017 – 8020; *Angew. Chem.* **2010**, *122*, 8190 – 8194.

[27] R. Haiges, J. A. Boatz, M. Yousufuddin, K. O. Christe, *Angew. Chem. Int. Ed.* **2007**, *46*, 2869 – 2874; *Angew. Chem.* **2007**, *119*, 2927 – 2932.

[28] R. Haiges, T. Schroer, M. Yousufuddin, K. O. Christe, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2691 – 2695.

[29] K. O. Christe in *Efficient preparations of fluorine compounds* (Ed.: H. W. Roesky), Wiley, Hoboken, NJ, **2013**, pp. 1 – 6.

[30] SAINT 8.27B, Bruker AXS Madison, WI, **2011**.

[31] SADABS 2012-1, Bruker AXS Madison, WI, **2012**.

[32] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122; b) SHELXL, 2012 – 4, G. M. Sheldrick, **2012**; c) SHELXTL, 2012.4-3, Bruker AXS Madison, WI, **2012**.

[33] L. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.