

Azide groups in high oxidation state Mn carboxylate chemistry: a new Mn_{11} complex and its conversion to a Mn_{25} azide complex with $Me_3SiN_3^\ddagger$

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A new high oxidation state $Mn^{III/IV}_{11}$ carboxylate complex has been prepared and then converted to a Mn^{III}_{25} azide/carboxylate cluster with Me_3SiN_3 ; the Mn_{25} product is the initial example of a higher oxidation state Mn azide complex not stabilized by any chelate ligands.

Higher oxidation state Mn carboxylate clusters have been the focus of much attention because of their relevance to many areas such as bioinorganic chemistry, catalysis, and materials science.¹ The latter includes the field of single-molecule magnets (SMMs),² which are molecules that can function as nanoscale magnets and which represent a molecular or ‘bottom-up’ approach to nanoscale magnetism.³ The best studied type of SMM is the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ ($Mn^{III}_8Mn^{IV}_4$; R = various) family, but a number of others have since been discovered, most of them in Mn carboxylate chemistry.⁴ As part of an ongoing search for new families of SMMs, we recently initiated a detailed study of the use of azide (N_3^-) groups in conjunction with alkoxide-based chelates in Mn^{III} carboxylate chemistry. This has successfully led to a variety of new high-spin molecules and SMMs,⁵ reflecting the known ability of the N_3^- ion, when bridging in the 1,1 (end-on) fashion, to be a mediator of ferromagnetic interactions for a wide range of M–N–M angles.⁶ In contrast, the presence of bridging azide groups in non-chelate Mn^{III} carboxylate chemistry is completely unknown. Nevertheless, as long as $\{Mn^{n+}_x(O_2CR)_y(N_3)_z\}$ species are inherently stable in the absence of stabilizing chelate groups, this area seemed to us to have the potential to be a rich source of new species of various nuclearities and structural types. We have thus sought to prepare Mn^{III} /azide/carboxylate compounds, and herein report the first success of this effort.

Developing successful entry into this chemistry proved very challenging. Several routes were explored using available Mn^{n+} ($n = 2, 3$) carboxylate sources and simple N_3^- salts, and employing methods such as (i) *in situ* comproportionation reactions between Mn^{II} and Mn^{VII} (i.e. MnO_4^-) reagents, (ii) reductive aggregation of Mn^{VII} under acidic conditions, and (iii) reactions of preformed Mn^{III} -containing clusters. However, in our hands these all led to azide-free products,

emphasizing the beneficial effect of the presence of chelates. We thus used Me_3SiN_3 , a reagent that has found previous employment in a dual role of azide delivery and carboxylate abstraction (as Me_3SiO_2CR), such as in the synthesis of a chelate-containing $Mn^{III}_3Mn^{IV}$ azide complex.⁷ We are investigating several such reactions with a variety of preformed Mn_x carboxylate complexes, and the breakthrough success came when we used an unpublished complex as starting material, so we report that here also.

The reaction of $Mn(O_2CPh)_2$, $NBu^t_4MnO_4$, $(NEt_4)MnCl_5$,⁸ and $PhCO_2H$ in a 4 : 1 : 4 : 32 molar ratio in hot $MeNO_2$ gave a dark brown solution. Slow evaporation of this solution over four days gave X-ray quality dark brown plate-like crystals of $[Mn_{11}O_{12}(O_2CPh)_{15}] \cdot PhCO_2H \cdot 2MeNO_2$ (**1**· $PhCO_2H \cdot 2MeNO_2$), which were isolated by filtration in 70% yield. Complex **1**· $PhCO_2H \cdot 2MeNO_2$ crystallizes in the monoclinic space group $P2_1/c$ with two crystallographically independent Mn_{11} molecules in the unit cell, but their interatomic distances and angles differ only marginally; thus, only the one containing atoms Mn12–Mn22 will be discussed in detail.† The structure† (Fig. 1, top) comprises 6 Mn^{IV} and 5 Mn^{III} atoms bridged by 12 μ_3-O^{2-} and 15 $\eta^1:\eta^1:\mu-PhCO_2^-$ groups; the latter provide the peripheral ligation about the central $[Mn_{11}O_{12}]^{15+}$ core. The latter is shown in Fig. 1 (bottom): it consists of a triangular arrangement of three dinuclear $[Mn^{IV}_2(\mu-O^{2-})_2]^{4+}$ units (Mn12/Mn14, Mn15/Mn17, Mn21/Mn22). There is a Mn^{III} atom (Mn13, Mn18, Mn20) lying on each edge of the triangle, attached to the $[Mn^{IV}_2(\mu-O^{2-})_2]^{4+}$ units at the $\mu-O^{2-}$ ions, which thus all become μ_3 . The remaining two Mn^{III} atoms (Mn16, Mn19) cap each side of the triangle, being attached to three μ_3-O^{2-} groups that each bridge a $Mn^{III}Mn^{IV}$ pair. The structure of the core can be alternatively described as consisting of the fusion of triangular $[Mn_3(\mu_3-O^{2-})]$ sub-units. Complex **1** possesses virtual D_3 point group symmetry. The Mn ions are all six-coordinate with near-octahedral geometry, and their assigned oxidation states were established by charge considerations, bond valence sum (BVS) calculations,⁹ and the expected Jahn–Teller (JT) distortions of the Mn^{III} ions, which take the form of axial elongations. BVS calculations were also performed on the inorganic μ_3-O atoms to confirm that none of them is a OH^- ion. It is also of interest to note that complex **1** possesses a rather high average oxidation state of +3.63, larger than the +3.33 for the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ family of clusters⁴ and the second highest for a polynuclear Mn_x species to date.¹⁰

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† Electronic supplementary information (ESI) available: Crystallographic data for **1**· $PhCO_2H \cdot 2MeNO_2$ and **2**·4MeCN, and various magnetism figures. CCDC 710291 and 710292. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b902016k

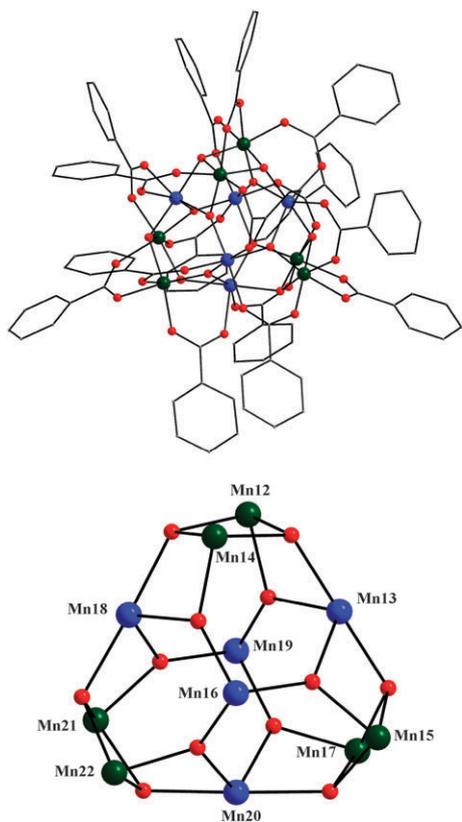


Fig. 1 (top) Pov-Ray representation of one of the two crystallographically independent molecules in **1**·PhCO₂H·2MeNO₂, with H atoms omitted for clarity; (bottom) the [Mn₁₁O₁₂]¹⁵⁺ core of **1**. Colour scheme: Mn^{III} blue; Mn^{IV} olive; O red; C grey.

Complex **1** has been employed as a starting material for various reactions with Me₃SiN₃. When a dark brown solution of dried **1**·PhCO₂H in MeCN was treated with 2 equiv. of Me₃SiN₃, there was a noticeable colour change to dark red. The solution was filtered and carefully layered with Et₂O. Brown crystals of [Mn₂₅O₂₀(N₃)₆(O₂CPh)₂₆(MeCN)₂·4MeCN (**2**·4MeCN) grew slowly over several days and were isolated by filtration; the yield was 15%.[†] Complex **2** turned out to be the desired initial example of a Mn^{III}-containing carboxylate complex possessing bridging azides. The structure[‡] of **2** (Fig. 2, top) comprises 22 Mn^{III} and 3 Mn^{II} atoms bridged by 8 μ₄- and 12 μ₃-O²⁻ ions to give a remarkable, nonplanar [Mn₂₅O₂₀]³²⁺ core. The core structure can be described as consisting of a central, near-planar Mn₇ unit comprising a Mn^{II} atom held within a Mn^{III}₆ hexagon by six μ₃-O²⁻ ions. The latter all become μ₄ by bridging to 4 Mn^{III} and 2 Mn^{II} atoms lying three each above and below the central [Mn^{III}₆Mn^{II}] disk, and are further linked to each other by two μ₄-O²⁻ ions. The resulting Mn₁₃ unit is held within a non-planar (puckered) ring of 12 Mn^{III} atoms by 12 μ₃-O²⁻ ions and 6 μ-1,1 (end-on) N₃⁻ groups; two of the latter bridge a Mn^{II}...Mn^{III} pair and four a Mn^{III}...Mn^{III} pair. The complex thus contains an overall [Mn₂₅(μ₄-O)₈(μ₃-O)₁₂(μ-N₃)₆]²⁶⁺ core (Fig. 2, bottom). Peripheral ligation about this core is provided by 20 η¹:η¹:μ, 3 η¹:η²:μ₃, and 3 η²:η²:μ₄ bridging PhCO₂⁻ groups and two terminal MeCN molecules. The mechanism of the conversion of **1** to **2** is clearly a very complicated one. In previous cases

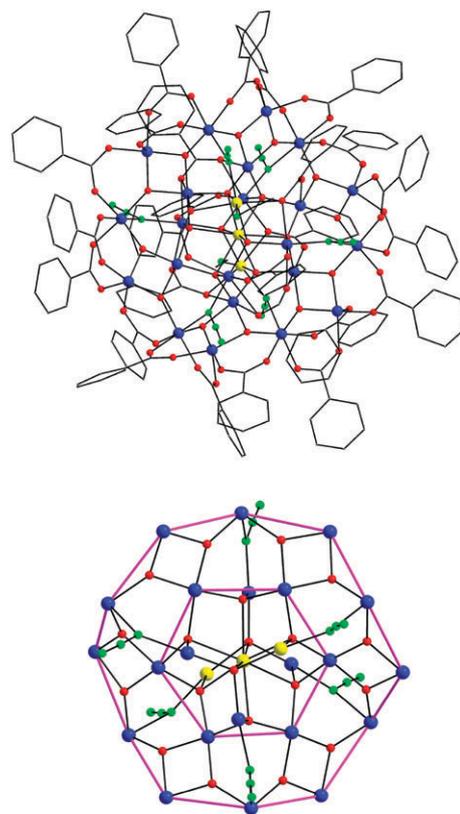


Fig. 2 The structure of **2** (top) and its [Mn₂₅O₂₀(N₃)₆]²⁶⁺ core (bottom), emphasizing with purple thick lines the outer Mn₁₂ and inner Mn₆ cyclic units. H atoms have been omitted for clarity. Colour scheme: Mn^{II} yellow; Mn^{III} blue; O red; N green; C grey.

where carboxylate abstraction has triggered structural changes in Mn₄ complexes, we have identified that disproportionation of Mn^{III} has occurred, and this may also be the case here, which would also rationalize the small yield of **2**. However, we have not isolated any other clean products from this reaction, and there is likely a complicated mixture of species in the filtrate.

Charge balance considerations, inspection of metric parameters, and BVS calculations⁹ confirmed the oxidation states and protonation levels of Mn and O²⁻ ions, respectively. All the Mn^{II} atoms except the central one, which is eight-coordinate with distorted dodecahedral geometry,¹¹ and twelve of the Mn^{III} atoms are six-coordinate with near-octahedral geometry. The remaining ten Mn^{III} atoms are five-coordinate with distorted square pyramidal geometry.

Solid-state dc (direct current) and ac (alternating current) magnetic susceptibility (χ_M) studies were performed on **1**·PhCO₂H and **2** in a 1 kG (0.1 T) dc field in the 5.0–300 K range, and with a 3.5 G ac field oscillating in the 1.8–15 K range at various frequencies, respectively. The obtained dc data are plotted as $\chi_M T$ vs. T in Fig. 3, and reveal predominantly antiferromagnetic exchange interactions in both **1**·PhCO₂H and **2**. $\chi_M T$ for **1**·PhCO₂H decreases from 17.33 cm³ K mol⁻¹ at 300 K to reach a plateau of ~11.6 cm³ K mol⁻¹ in the 50–90 K range, and then increases to 12.07 cm³ K mol⁻¹ at 20.0 K before dropping to 11.24 cm³ K mol⁻¹ at 5.0 K. The decrease at the lowest

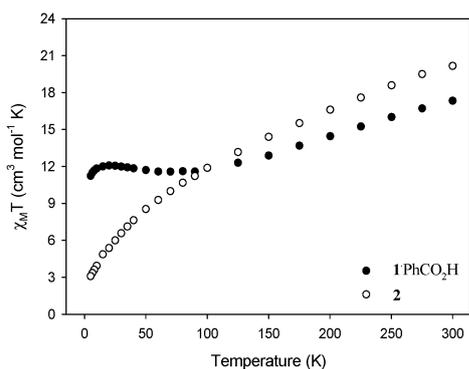


Fig. 3 $\chi_M T$ vs. T plots for complexes **1**-PhCO₂H (●) and **2** (○).

temperatures is likely due to a combination of Zeeman effects, zero-field splitting and any weak intermolecular interactions. The overall shape of the curve and its low temperature value suggest a relatively large ground-state spin value for **1** of $S \approx 5$, probably with low-lying excited states as expected for a high nuclearity, spin frustrated system; the spin frustration is consistent with the many triangular units within the core topology of **1**. For **2**, $\chi_M T$ steadily decreases from 20.16 cm³ K mol⁻¹ at 300 K to 3.09 cm³ K mol⁻¹ at 5.0 K, indicating predominantly antiferromagnetic interactions leading to a much smaller ground state S value.

An alternative determination of S and a probe of the magnetization relaxation dynamics for **1**-PhCO₂H and **2** can be obtained from ac susceptibility measurements,¹² which preclude complications from a dc field and/or low-lying excited states. Extrapolation of the in-phase $\chi_M' T$ vs. T plot of **1**-PhCO₂H from above ~ 7 K down to 0 K gives a value of ~ 13.6 cm³ K mol⁻¹, suggesting an $S = 5$ ground state with $g \sim 1.9$, below 2.0 as expected for Mn. The corresponding plot for **2** shows a rapid decrease below 15 K and appears to be heading for $\chi_M' T \sim 3$ cm³ K mol⁻¹ at 0 K, consistent with a low $S \sim 3/2$ ground state with very low-lying excited states, as expected for such a high nuclearity complex. At lower temperatures, **1**-PhCO₂H displays a frequency-dependent decrease in $\chi_M' T$ and a concomitant appearance of out-of-phase χ_M'' signals whose peak maxima are located below the operating limit of our magnetometer (1.8 K). Such signals are indicative of the superparamagnet-like slow relaxation of an SMM, albeit with a small barrier. As a result of the latter, micro-SQUID studies would be required at very low temperatures (<1 K) in order to detect whether **1** (and perhaps **2**) exhibit magnetization hysteresis loops.

In conclusion, the present work represents the initiation of a distinct and currently unexplored sub-area of Mn cluster chemistry, namely Mn^{III}-azides with no organic ligands other than carboxylates. The prototype complex is **2**, a Mn₂₅/RCO₂⁻/N₃⁻ species with a remarkable structure that was obtained using Me₃SiN₃. In addition, we report an unusually high oxidation state Mn₁₁ cluster (**1**) from which **2** was obtained. Complexes **1** and **2** join only a very small group of known Mn₁₁^{7,13} and Mn₂₅¹⁴ clusters, and are very different from the others in their core topologies and metal oxidation

levels. While the absence of stabilizing chelate ligands has made entry into this area of Mn chemistry more difficult to achieve, the structural beauty of the prototype Mn/RCO₂⁻/N₃⁻ complex suggests the effort was worth it and that an interesting new area of Mn cluster chemistry has been opened up. We are currently continuing to investigate the products from the use of Me₃SiN₃ with other preformed, high-valent Mn^{III,IV}_{*x*} and/or Mn^{III,IV}_{*x*}Ce^{IV}_{*y*} species.

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Notes and references

‡ Vacuum-dried solid analysed as **1**-PhCO₂H. Calcd. (found): C, 49.18 (49.36); H, 2.99 (2.85%). Dried solid analysed as solvent-free **2**. Calcd. (found): C, 43.16 (43.06); H, 2.65 (2.35); N, 5.41 (5.55%). Crystal data for **1**-PhCO₂H-2MeNO₂: C₁₁₄H₈₇Mn₁₁N₃O₄₈, $M_w = 2857.27$, monoclinic, space group $P2_1/c$ with $a = 28.247(3)$, $b = 26.842(3)$, $c = 31.920(4)$ Å, $\beta = 104.655(3)^\circ$, $V = 23414(5)$ Å³, $T = 173(2)$ K, $Z = 8$, 105 514 reflections collected, 30 616 unique ($R_{int} = 0.1344$), $R1 [I > 2\sigma(I)] = 0.0826$, $wR2 = 0.1862$ (F , all data). CCDC 710291. Crystal data for **2**-4MeCN: C₁₉₄H₁₄₈Mn₂₅N₂₄O₇₂, $M_w = 5340.86$, triclinic, space group $P\bar{1}$ with $a = 20.3146(12)$, $b = 20.3315(12)$, $c = 27.2029(15)$ Å, $\alpha = 86.097(1)$, $\beta = 76.095(1)$, $\gamma = 78.658(1)^\circ$, $V = 10690.7(11)$ Å³, $T = 173(2)$ K, $Z = 2$, 70 649 reflections collected, 47 852 unique ($R_{int} = 0.1044$), $R1 [I > 2\sigma(I)] = 0.0598$, $wR2 = 0.1129$ (F , all data). CCDC 710292.

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