Syntheses and Properties of Metal-Centered Mixed-Valent $[NEt_4]\{Mn^{II}\subset[Mn^{II}_3Mn^{III}_3Cl_6(L)_6]\}$ Manganese Wheels[‡]

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In memoriam Professor Bernd A. Heß

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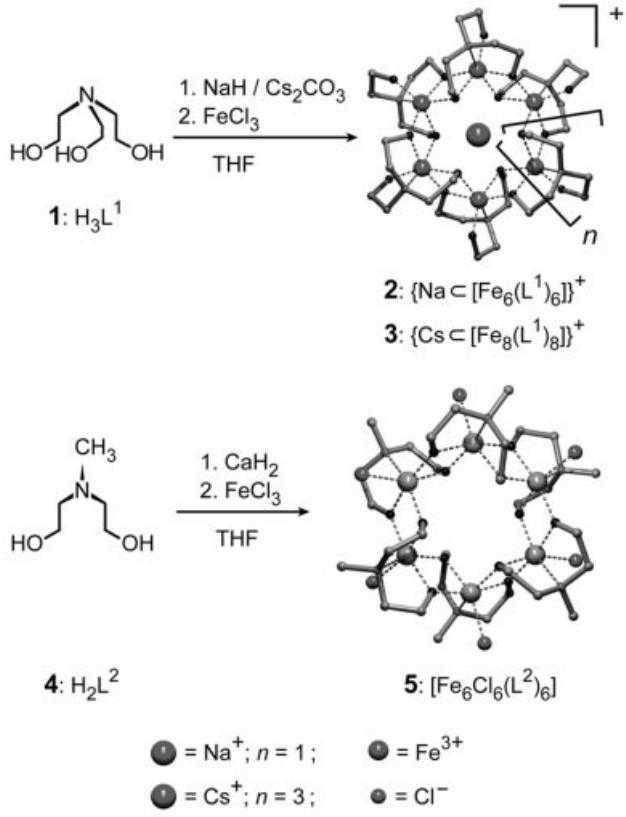
Upon reaction of *N*-substituted diethanolamines H_2L^{2-4} (**4**, **6**, **7**) with cesium carbonate and bis(tetraethylammonium) tetrachloromanganate(II) in acetonitrile in the presence of air, the metal-centered mixed-valent manganese wheels $[NEt_4]\{Mn^{II}\subset[Mn^{II}_3Mn^{III}_3Cl_6(L^{2-4})_6]\}$ (**8**–**10**) were generated. X-ray crystallographic structure analyses revealed, that **8**–**10** are principally isostructural and consist of an alternating ring of three Mn^{II} and three Mn^{III} ions, centered by an additional Mn^{II} ion. The cyclic voltammograms of **8** and **10** displayed three quasi-reversible oxidation processes, which are attributed to the subsequent one electron-oxidations of the three peripheral Mn^{II} ions to Mn^{III}. Oxidation of the central Mn^{II} ion is not observed within the applied potential.

Introduction

Despite their unpredictable nature, polyoxometalates have become the focus of intense research activities.[2] Recently, distinct supramolecular metal clusters have become accessible by rational design rather than by serendipity[3] and oxo-bridged polynuclear iron and manganese metal clusters have been the subject of numerous detailed magnetic studies, which have been rewarded by the discovery of single molecule magnets (SMMs).[4,5] In this context, we reported on the template-mediated self-assembly of six- and eight-membered iron-coronates, $\{Na\subset[Fe_6(L^1)_6]\}^+$ (**2**) and $\{Cs\subset[Fe_8(L^1)_8]\}^+$ (**3**), which were prepared from triethanolamine H_3L^1 (**1**) with iron(III) chloride and sodium hydride or cesium carbonate, respectively (Scheme 1).[6] A common feature of complexes **2** and **3** is that the μ_1-oxygens of the $(L^1)^{3-}$ ligands do not participate in the formation of the hexa- or octanuclear structures. They solely function as ligands for the coordinative saturation of the iron centers. For this reason, further mono-anionic donors, such as chloride ions, should also be candidates for this function. Therefore, reaction of *N*-methyldiethanolamine H_2L^2 (**4**) with cal-



Scheme 1. Top: Synthesis of ferric wheels **2** and **3** with triethanolamine. Bottom: Synthesis of ferric wheel **5** with *N*-methyldiethanolamine.

[‡] Chelate Complexes, Part 28. Part 27: Ref.[1]

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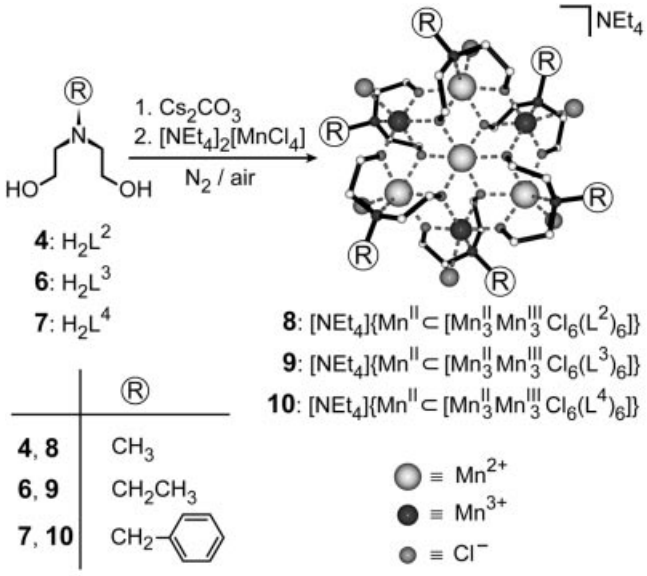
cium hydride and iron(III) chloride yielded the unoccupied neutral iron coronand $[Fe_6Cl_6(L^2)_6]$ (**5**) (Scheme 1).[6] In **5**, the μ_2-oxygen donors of the $(L^2)^{2-}$ ligands are structure determining, whereas their *N*-methyl groups are not. In addition, six chloride coligands are necessary for coordinative saturation at the iron centers and for charge compensation. Consequently, a series of ferric wheels was generated with *N*-substituted diethanolamines.[1,7]

In this communication we report on the synthesis of metal-centered, heptanuclear, mixed-valent manganese wheels **8**–**10**.

Results and Discussion

Synthesis

The metal-centered, heptanuclear, mixed-valent, six-membered manganese wheels **8**–**10** were generated in good yields in a one-pot reaction. For that purpose, *N*-substituted diethanolamines **4**, **6** and **7** were deprotonated with cesium carbonate in acetonitrile under nitrogen for 1 h. After addition of soluble bis(tetraethylammonium) tetrachloromanganate(II), the resulting reaction mixture was stirred for an extra 4 d. Workup in air, and crystallization from suitable solvent systems afforded black parallelepipeds (Scheme 2).



Scheme 2. Synthesis of manganese wheels **8**–**10** with *N*-substituted diethanolamines.

X-ray Analyses

X-ray crystallographic structure determinations were carried out for **8**–**10** (Table 2).[8,9] According to these analyses all three clusters are principally isostructural with idealized S_6 molecular symmetry, and for that reason, only the structure of **8** is discussed in detail. In the crystal, **8** is present as a cyclic manganese complex, consisting of an alternating ring of three Mn^{II} and three Mn^{III} ions[10] centered by an additional Mn^{II} ion, and tetraethylammonium is the counterion. Charge considerations and bond valence calculations require six doubly deprotonated methyldiethanolate amine ligands and six chloride ions. For the idealized consideration, the six equivalent manganese ions of the centrosymmetric anion $\{Mn^{II} \subset [Mn^{II}_3 Mn^{III}_3 Cl_6(L^2)_6]\}^-$ of **8** are located in the corners of a regular hexagon. The Mn–Mn distance is 3.3 Å. The diameter of the hexagon, defined as

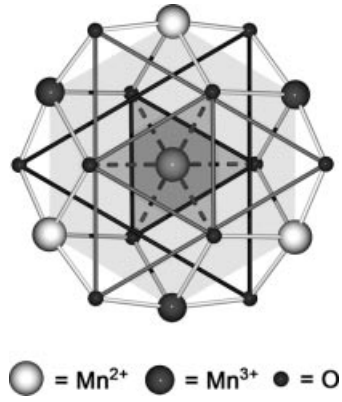


Figure 1. Schematic presentation of the central $[Mn^{II}_3 Mn^{III}_3 \mu_2\text{-}O_6]$ scaffold of $[\mathbf{8}]^-$ together with the octahedral μ_3-O environment of the encapsulated Mn^{II} ion. View along the idealized molecular S_6 axis, neglecting the valency of manganese.

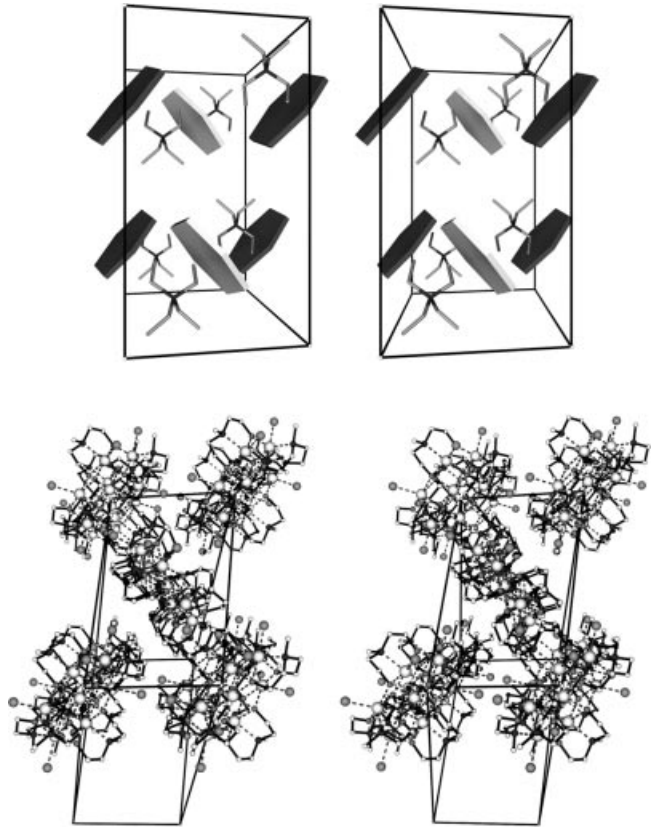


Figure 2. Top: Schematic stereo presentation of the crystal packing of **8** along the *a* axis. Bottom: Stereo view of the crystal packing of manganese wheel **8** along the *a*,*b* plane diagonal of the unit cell.

the distance between two opposite manganese ions, is 6.6 Å. The distorted octahedral coordination sphere of the manganese ions is composed of one nitrogen donor, two μ_2- and two μ_3-oxygen donors and one chloride ion. Consequently, doubly deprotonated methyldiethanolate amine acts as a tetratope tridentate ligand and links three manganese ions. There is a set of six outer μ_2-O donors and a set of six inner μ_3-O donors. The six oxygen donors of each set are located at the corners of a pair of regular triangles, rotated by 60° relative to each other. The pairs of triangular faces are arranged parallel and equidistant in pairs from the central one, with one plane above and one below this hexagonal plane, generated by the peripheral manganese ions. These two pairs of six oxygen donors are related by an S_6 axis. The Mn^{II} ion located in the center of $[\mathbf{8}]^-$ has a distorted octahedral coordination sphere with respect to the six μ_3-O donors (Figure 1). The diameter of the cavity d[11] marked by opposite μ_3-O donors almost corresponds to double the ionic radius of Mn^{II}.

Manganese wheel $[NEt_4]\{Mn^{II}\subset[Mn^{II}_3Mn^{III}_3Cl_6(L^2)_6]\}$ (**8**) crystallizes with four molecules in the unit cell. The disklike clusters are all arranged in parallel (shortest midpoint distance d = 11.2 Å), but in two orientations (mean included angle φ = 85°), and are piled in cylindrical columns, with all the manganese centers superimposed (Figure 2).

Cyclic Voltammetry

The cyclic voltammogram of **8** and **10** were recorded under anaerobic and aprotic conditions and displayed three quasi-reversible oxidation processes, which are attributed to the subsequent one-electron oxidations of the three Mn^{II} ions to Mn^{III}, which are located at the ring positions (Figure 3, Table 1). Oxidation of the central Mn^{II} ion is not observed within the applied potential range.[12] In multisweep experiments under thin layer conditions the first oxidation shows complete reversibility over several cycles, whereas the second and third oxidations lead to degradation of the complex indicating irreversible chemical side reactions. The large potential displacement between the individual oxidations of several hundred mV is indication of a strong electronic coupling between the crystallographically equivalent manganese ions, whereas in a noncoupled system a simultaneous threefold oxidation within one oxidation wave would have been expected.

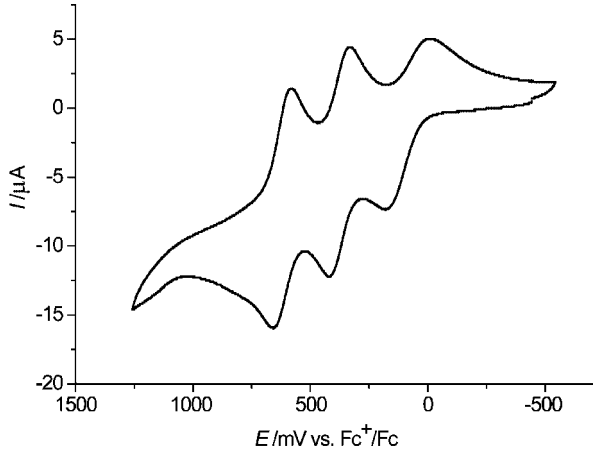


Figure 3. Cyclic voltammogram of **8**.

Table 1. Data of the cyclic voltammogram of **8** and **10** in CH_3CN {0.1 M $[(n\text{Bu})_4N](PF_6)$} versus Fc/Fc^+ at 20 °C; scan rate 200 mV s^{-1}.

Complex	$E_{1/2}{}^1$ [mV]	$E_{1/2}{}^2$ [mV]	$E_{1/2}{}^3$ [mV]
8	85	375	630
10	119	396	650

Conclusion

We are still far from understanding the template effect on the mysterious rules of the self-assembling processes leading to metallic wheels. Whereas triethanolamine with iron(III) chloride affords homovalent metal-centered cationic wheels like $\{Na\subset[Fe_6(L^1)_6]\}^+$ (**2**), methyldiethanolamine yields the unoccupied neutral homovalent species $[Fe_6Cl_6(L^2)_6]$ (**5**). However, when manganese(II) instead of iron(III) was reacted under aerobic conditions with methyldiethanolamine, the mixed-valent metal-centered anionic wheel $\{Mn^{II}\subset[Mn^{II}_3Mn^{III}_3Cl_6(L^2)_6]\}^-$ $(\mathbf{8})^-$ was formed.

Experimental Section

General Techniques: Metal salts, and H_2L^2[2,3] (**4**, **6**) were used as obtained from Aldrich. All solvents used were purified and dried according to standard procedures. $[NEt_4]_2[MnCl_4]$ and H_2L^4 (**7**) were prepared according to literature methods.[13,7] IR spectra were recorded from KBr pellets with a Bruker IFS 25 spectrometer. FAB-MS spectra were recorded with a Micromass ZAB-Spec spectrometer. Elemental analyses were performed with an EA 1110 CHNS-Microautomat. Single-crystal X-ray structure analyses: details for crystal data, data collection and refinement are given in Table 2. X-ray data for **8**–**10** were collected with a Nonius Kappa CCD area detector, using Mo-K_α radiation (λ = 0.71073 Å). Scalepack absorption correction was employed. The structure was solved by direct methods with SHELXS-97 and refined with full-matrix least-squares against F^2 with SHELXL-97.[8]

General Method: Methyldiethanolamine H_2L^2 (**4**) (1.7 mmol, 0.200 g), ethyldiethanolamine H_2L^3 (**6**) (1.7 mmol, 0.230 g), or benzyldiethanolamine H_2L^4 (**7**) (1.7 mmol, 0.330 g) were added to a suspension of Cs_2CO_3 (2 mmol, 0.650 g) in CH_3CN (70 mL). After stirring for 1 h at room temperature $[NEt_4]_2[MnCl_4]$ (2 mmol, 0.915 g) was added. The reaction mixture was stirred for 4 d at room temperature. For **8** and **9**, the resulting black precipitate was filtered off, extracted with $CHCl_3$ (100 mL) and concentrated. Black crystals were obtained from $CHCl_3/Et_2O$ (for **8**) or CH_3CN/Et_2O (for **9**). For **10**, the resulting black suspension was filtered, and the filtrate was concentrated in vacuo to dryness. A mixture of Et_2O (5 mL) and EtOH (5 mL) was added. After standing for 12 h, the black precipitate that had formed was filtered off and extracted with $CHCl_3$ (100 mL). Black crystals were obtained from $CHCl_3/Et_2O$.

Table 2. Details of X-ray structure determinations for complexes **8**–**10**.

	8	**9**	**10**
Formula	$C_{38}H_{86}Cl_6Mn_7N_7O_{12}$	$C_{44}H_{98}Cl_6Mn_7N_7O_{12}$	$C_{74}H_{110}Cl_6Mn_7N_7O_{12}\cdot 7\,CHCl_3$
*M*r	1430.42	1514.57	2722.55
Crystal size (mm)	0.30 × 0.30 × 0.10	0.30 × 0.30 × 0.20	0.35 × 0.30 × 0.15
Crystal system	monoclinic	cubic	monoclinic
Space group	*C*2/*c*	*Pa*3	$P2_1$
T [K]	173(2)	173(2)	173(2)
a [Å]	30.4649(13)	18.600(2)	13.917(3)
b [Å]	18.9810(11)		25.151(5)
c [Å]	11.1999(5)		16.410(3)
α [°]			
β [°]	107.237(3)		96.82(3)
γ [°]			
V [Å^3]	6185.5(5)	6434.3(13)	5703(2)
Z	4	4	2
$\rho_{calcd.}$ [Mg m^{-3}]	1.536	1.563	1.585
θ range [°]	2.12 to 24.99	2.19 to 27.45	1.25 to 27.47
Reflections collected	9455	4636	21343
Unique reflections	5427	2460	21343
[R_{int}]	0.0348	0.0256	0.0000
Reflections observed [$I > 2\sigma(I)$]	3706	1682	15862
Parameters	318	126	1208
Final *R*1 [$I > 2\sigma(I)$]	0.0673	0.0557	0.0614
*wR*2 (all data)	0.2451	0.1755	0.1786
Largest residuals [e Å^{-3}]	1.971/–0.706	1.217/–0.554	1.499/–1.186

Compound [NEt$_4$]{Mn^{II}⊂[Mn$^{II}_3$Mn$^{III}_3$Cl$_6$(L^2)$_6$]} (8): Starting material: H_2L^2, $MeN(CH_2CH_2OH)_2$ (**4**): Yield 153 mg (32%) black crystals from chloroform/Et_2O; m.p. > 250 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3464, 2855, 2363, 2345 cm^{-1}. FAB-MS (*m*-NBA): *m*/*z* (%) = 1394 (5) $[NEt_4][Mn_7Cl_5(L^2)_6]^+$, 1300 (15) $[Mn_7Cl_6(L^2)_6]^+$, 1265 (40) $[Mn_7Cl_5(L^2)_6]^+$, 1229 (40) $[Mn_7Cl_4(L^2)_6]^+$, 1146 (40) $[Mn_7Cl_6(L^2)_5]^+$, 1100 (40) $[Mn_7Cl_5(L^2)_5]^+$, 1075 (50) $[Mn_7Cl_4(L^2)_5]^+$, 1030 (100) $[Mn_7Cl_6(L^2)_4]^+$. $C_{38}H_{86}Cl_6Mn_7N_7O_{12}$ (1430.42): calcd. C 31.91, H 6.06, N 6.85; found C 31.59, H 6.06, N 6.76.

Compound [NEt$_4$]{Mn^{II}⊂[Mn$^{II}_3$Mn$^{III}_3$Cl$_6$(L^3)$_6$]} (9): Starting material: H_2L^3, $EtN(CH_2CH_2OH)_2$ (**6**): Yield 212 mg (42%) black crystals from CH_3CN/Et_2O; m.p. > 250 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3434, 2969, 2936, 2903, 2856, 1623 cm^{-1}. FAB-MS (*m*-NBA): *m*/*z* (%) = 1515 (5) $[NEt_4][Mn_7Cl_6(L^3)_6]^+$, 1478 (5) $[NEt_4][Mn_7Cl_5(L^3)_6]^+$, 1382 (20) $[Mn_7Cl_6(L^3)_6]^+$, 1349 (60) $[Mn_7Cl_5(L^3)_6]^+$, 1313 (70) $[Mn_7Cl_4(L^3)_6]^+$, 1218 (50) $[Mn_7Cl_5(L^3)_5]^+$, 1181 (50) $[Mn_7Cl_4(L^3)_5]^+$, 1145 (60) $[Mn_7Cl_3(L^3)_5]^+$, 1085 (100) $[Mn_7Cl_5(L^3)_4]^+$. $C_{44}H_{98}Cl_6Mn_7N_7O_{12}$ (1514.57): calcd. C 34.89, H 6.52, N 6.47; found C 33.80, H 6.67, N 6.13.

Compound [NEt$_4$]{Mn^{II}⊂[Mn$^{II}_3$Mn$^{III}_3$Cl$_6$(L^4)$_6$]} (10): Starting material: H_2L^4, $BnN(CH_2CH_2OH)_2$ (**7**): Yield 277 mg (44%) black crystals from chloroform/Et_2O; m.p. > 250 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3548, 3028, 2904, 2858, 2367 cm^{-1}. FAB-MS (*m*-NBA): *m*/*z* (%) = 1887 (5) $[NEt_4][Mn_7Cl_6(L^4)_6]^+$, 1850 (10) $[NEt_4][Mn_7Cl_5(L^4)_6]^+$, 1755 (10) $[Mn_7Cl_6(L^4)_6]^+$, 1720 (20) $[Mn_7Cl_5(L^4)_6]^+$, 1685 (15) $[Mn_7Cl_4(L^4)_6]^+$, 1527 (20) $[Mn_7Cl_5(L^4)_5]^+$, 1334 (50) $[Mn_7Cl_5(L^4)_4]^+$, 1030 (20) $[Mn_5Cl_5(L^4)_3]^+$. $C_{74}H_{110}Cl_6Mn_7N_7O_{12}\cdot 7\,CHCl_3$ (2722.55).[14]

Acknowledgments

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[9] CCDC-247134 (**8**), CCDC-247135 (**9**) and CCDC-247133 (**10**) 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.

[10] The alternation of Mn^{II} and Mn^{III} ions in **8**–**10** is explicitly confirmed by the coordination geometry of the Mn^{II} and Mn^{III} centers in compound **10**; cf.: CCDC-247133.

[11] $d = d_{\mu3O-\mu3O} - 2r_O = 4.4 - 2.3$ Å almost corresponds to double the ionic radius (1.9 Å) of high-spin Mn^{II}.

[12] Cf.: a) M. Ruben, J. Rojo, F. J. Romero-Saluero, L. H. Uppadine, J.-M. Lehn, *Angew. Chem.* **2004**, *116*, 3728–3747; *Angew. Chem. Int. Ed.* **2004**, *43*, 3644–3662; b) L. Zhao, C. J. Matthews, K. Thompson, S. L. Heath, *Chem. Commun.* **2000**, 265–266.

[13] N. S. Gill, R. S. Nyholm, *J. Chem. Soc.* **1959**, 3997–4007.

[14] The microanalytical data for **10** deviate from theory due to varying amounts of crystal solvents and are not recorded here.

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